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Isolation or Concentration of Organic Substances from Water - An Evaluation of Reverse Osmosis Concentration

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ISOLATION OR CONCENTRATION OF ORGANIC SUBSTANCES FROM WATER--

An Evaluation of Reverse Osmosis Concentration

by

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68-03-2999

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16. ABSTRACT

This study describes the development and evaluation of a reverse osmosis (RO)/Donnan dialysis system to be used in the preparation of drinking water concentrates for biological testing. Two reverse osmosis membranes, cellulose acetate (Osmonics, Inc.) and FT-30 (Film Tec, Inc.), were selected for laboratory evaluation, primarily because of their purported short-term chlorine resistance. Two Donnan membranes, Nafion® (Dupont) and MA 3475 (IONAC), were chosen for further study based upon their chemical resistance characteristics (chlorine, caustic, and acid tolerance). The FT-30 membrane, a thin-film composite, demonstrated a substantially greater rejection efficiency for the model compounds than the cellulose acetate membrane. As expected from the rejection data, the recoveries of model solutes were much better for the FT-30 membrane system than the cellulose acetate system. Overall the recovery values (2-74%) were poor for the majority of model compounds in both RO systems and substantially less than anticipated based on the rejection data.

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FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The complexities of environmental problems originate in the deep interdependent relationships between the various physical and biological segments of man's natural and social world. Solutions to these environmental problems require an integrated program of research and development using input from a number of disciplines. The Health Effects Research Laboratory, Research Triangle Park, NC and Cincinnati, OH, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. Wide ranges of pollutants known or suspected to cause health problems are studied. The research focuses on air pollutants, water pollutants, toxic substances, hazardous wastes, pesticides, and non-ionizing radiation. The laboratory participates in the development and revision of air and water quality criteria and health assessment documents on pollutants for which regulatory actions are being considered. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of environmental regulatory decisions involving the protection of the health and welfare of all U.S. inhabitants.

This report presents the results obtained during the development and evaluation of reverse osmosis/Donnan dialysis for the isolation and concentration of trace organic substances from water. Methods for the trace enrichment of organic contaminants in water are essential in determining potential health problems associated with waterborne organic contaminants since existing *in vivo* and *in vitro* biological test systems lack the necessary sensitivity for testing water samples as is.

F. Gordon Hueter, Ph.D.
Director
Health Effects Research Laboratory

ABSTRACT

A laboratory study, EPA Contract No. 68-03-2999, was performed to expand basic understanding of the reverse osmosis concentration method as applied to collection and concentration of trace organic chemicals from water. This knowledge will be invaluable in improving the efficiency of a proven method for preparing concentrated samples for health effects testing.

Commercially available reverse osmosis and Donnan membranes were surveyed for applicability to the reverse osmosis concentration method used by GSRI to collect organic concentrates. Two reverse osmosis membranes, cellulose acetate (Osmonics, Inc.) and FT-30 (Film Tec, Inc.), were selected for laboratory evaluation, primarily because of their purported short-term chlorine resistance. Two Donnan membranes, Nafion^{R} (Dupont) and MA 3475 (Ionac), were chosen for further study based upon their chemical resistance characteristics (chlorine, caustic, and acid tolerance).

Tests were performed to determine basic rejections of specific trace organic chemicals by the reverse osmosis membranes, and the FT-30 membrane was shown to have substantially better performance thn the cellulose acetate membrane. The effect of humic acid on the rejection of model compounds by the reverse osmosis membranes was evaluated and found not to be significant under the study conditions. The ability of Donnan membranes to retain specific organic solutes under operating conditions similar to those which might be required in actual sampling conditions was also assessed.

System blanks were examined for leachable organic compounds by gas chromatography/mass spectrometry (GC/MS), gas chromatography with electron capture (GC/ECD) and flame ionization detection (GC/FID). Leachables were examined with water and water plus hypochlorite as the recirculating test fluid. The test revealed very few leachable compounds for any of the membrane systems in the absence of chlorine. The three membranes normally used in field sampling (cellulose acetate, FT-30, and Nafion^{R}), where chlorine disinfectant levels are usually the highest, showed the least effects from chlorine exposure. Only one chlorinated product was detected in the test on the FT-30 membrane. Artifacts were produced in the blank run using the MA 3475 anion exchange membrane when stressed with chlorine; therefore, precautions against chlorine should be considered in the use of this membrane.

The cellulose acetate and FT-30 reverse osmosis membranes were used in conjunction with the Nafion^{R} Donnan membrane to concentrate 500 liters to 10 liters, a 50-fold (volumetric) concentration. The FT-30 membrane test was repeated in the presence of humic acid to determine its effect under concentration conditions. Solute recoveries and mass balances were calculated for the three concentration trials. Generally, the results of the mass balance determinations were good, when corrected for adsorption losses and considering the magnitude of the analytical task and problems associated with analysis. As expected from the rejection data, the recoveries were much better for the FT-30 membrane system than for the cellulose

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acetate system. Even though better recoveries were observed in early tests of the Nafion^R membrane with humic acid present, this effect was not observed in the concentration experiments, where it was apparently masked by other factors such as adsorption or lack of precision in analytical data.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

CA	--cellulose acetate
CF	--concentration factor (volumetric)
EPA	--Environmental Protection Agency
FT-30	--proprietary thin film composite membrane (Film Tec, Inc.)
GC/ECD	--gas chromatography with electron capture detection
GC/FID	--gas chromatography with flame ionization detection
GC/MS	--gas chromatography/mass spectrometry
GSRI	--Gulf South Research Institute
HPLC	--high performance liquid chromatography
LSI	--Langelier saturation index
MA 3475	--anion exchange membrane (Ionac)
mM	--millimolar
Nafion^{R}	--cation exchange membrane (Dupont)
OFW	--organic free water
PA	--polyamide
PBIL	--polybenzimidazole
PEI	--polyethyleneimine
PVF	--polyvinylfluoride
RO	--reverse osmosis
SOP	--standard operating procedure
TDS	--total dissolved solids
THM	--trihalomethane
TOC	--total organic carbon
XAD	--absorbent resin

SYMBOLS

C_i^F	initial feed (concentrate) concentration
C_f^F	final feed (concentrate) concentration
C^P	permeate concentration
C_f^S	final salt concentration
$\bar{C}_f^F$	projected final feed (concentrate) concentration
F	feed solution (used interchangeably for concentrate)
M_i^F	initial feed (concentrate) mass

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M_f^F	final feed (concentrate) mass
M_f^S	final mass in salt "pump" solution
M_F^{ads}	mass adsorbed
M^P	mass permeated
$\hat{M}_i^F$	initial mass corrected for losses due to adsorption
P	permeate solution
$\bar{\%}$	typical percentage solute loss due to adsorption (see Table 39)
R	membrane rejection
S	salt solution
V_i^F	initial feed (concentrate) volume
V_f^F	final feed (concentrate) volume
V_f^S	final salt solution volume
$F_{CF=X}$	feed sample of concentration factor = X
$P_{CF=X}$	permeate sample at concentration factor = X

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SECTION 1

INTRODUCTION

The study reported here, "Isolation or Concentration of Organic Substances From Water - An Evaluation of Reverse Osmosis Concentration" (EPA Contract No. 68-03-2999), is one of five companion studies funded in 1980 by EPA. The program objectives were to develop a better basic characterization of the reverse osmosis concentration method and to provide an experimental structure whereby the reverse osmosis method could be compared more directly with other methods for preparing concentrated samples of trace organics from drinking water. The ultimate use of the methodology is the preparation of samples for health effects testing. Alternate methodologies being evaluated by other investigators include adsorbent resins, vacuum distillation, powdered teflon, and supercritical fluid CO_2 extraction.

The reverse osmosis concentration method has been used to prepare concentrates under several EPA tasks (EPA Contract Nos. 68-03-2090, 68-03-2194, 68-03-2367, 68-03-2464, 68-03-2550, and 68-03-2713). The method involves repetitive batch concentrations using a reverse osmosis membrane to retain organics and reduce the sample volume (with an accompanying increase in concentration) by discarding water that permeates the membrane. The Donnan dialysis process has been used in many of the concentrations to minimize solids precipitation resulting from the increase in inorganic salt concentrations. Prior to the subject study, total organic carbon (TOC) measurements have been used to monitor the progress of the concentration. Although TOC is a convenient tool for measuring the gross organic content, it is a nonspecific measurement and provides little information on specific chemical solutes. Specific solutes (model compounds), representing classes of organic compounds, were evaluated to provide an indication of organic recovery.

Several other questions were unanswered at the beginning of this program:

1. Do the newer, "improved" membranes which have been commercialized in the last few years hold promise of improved organic recovery when used with the reverse osmosis concentration method?
2. What is the effect of typical drinking water (humic acid) levels on trace organic compound recovery?
3. What kinds of trace organics might leach from the membrane system into the concentrate?

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4. What effect do commonly encountered levels of chlorine have on the membrane performance, degradation, and possible subsequent contamination by newly generated substances?

5. What level of organic solute recovery can be expected from the reverse osmosis concentration system, and can mass balance analysis provide an assessment of the magnitude and sources of solute losses from the system?

6. What might be done operationally to improve the recoveries of the reverse osmosis concentration method?

It must be appreciated from the outset that the conduct of this study was more of an analytical chemistry challenge than a membrane evaluation. The task of measuring trace organic solutes at levels very near absolute detection limits and in complex water matrices containing varying loadings of acetone, humic acid, and mixed inorganic salts proved to be formidable. Three of the original target solutes had to be dropped altogether due to a lack of adequate analytical methodology. There were occasions when certain samples from a test series could not be assayed for particular problem compounds. Despite these obstacles and the frequent desire to have higher accuracy and lower detection limits, much useful information has been obtained from these tests. The following report describes the tests conducted, data generated, and the conclusions derived from the tests.

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SECTION 2

CONCLUSIONS

The completion of this evaluation of the reverse osmosis methodology provided much needed insight into several important aspects of the sampling method. Relevant conclusions summarized here are again restated in the recommendations as suggested changes for field sampling procedures. These changes should improve the overall recovery of trace organic compounds.

A survey of commercially available reverse osmosis and Donnan membranes was completed, and four membranes with potential utility in the reverse osmosis method were selected for evaluation in laboratory tests: two reverse osmosis (cellulose acetate and FT-30), one cation exchange (Nafion^{R}), and one anion exchange membrane (MA 3475).

The study demonstrated that with the FT-30 membrane system, the majority of solutes were concentrated in the reverse osmosis process. Lower enrichments were observed for those solutes that were adsorbed by the system. Solute concentration factors with the cellulose acetate system were lower in all cases than with the FT-30 system. This may be attributed in part to the requirement for using acetone as a co-solvent to achieve the solubility of the specified solutes.

System losses due to adsorption must be considered in mass balance determinations. The adsorption of some solutes may be concentration dependent, but concentration dependence was not examined during this study. It will be recommended that the adsorption phenomenon be examined in further detail in future work. Additional information in this area will help determine to what extent the adsorptive demands may be satisfied. The system demands for certain solutes may be satisfied by preconditioning the membrane system with the intended source water during field application of the method. Data from the system blanks and leaching study results indicate this adsorption phenomenon may be reversible to some extent.

Examination of the system blank samples revealed sporadic occurrences of the model solutes used for method evaluation. No pattern was found to these occurrences, which indicated that this was not a significant source of contamination and confirmed that the flushing regimes used in the study were adequate. A detailed examination of the system blanks using GC/MS methodology revealed no major sources of contamination from any of the membranes in the absence of chlorine. In the presence of chlorine, an increase in the number of organic compounds found in the system blanks was observed for all membrane systems, but only the anion exchange membrane exhibited what might be considered a deleterious effect.

The two reverse osmosis membranes and the Nafion^{R} membrane were tested for the effects that humic acid had on the rejection and recovery of the

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other model compounds. The Nafion^{R} membrane studies indicated an improved concentration in early screening tests, but when integrated into a concentration trial, the effect was not evident. This is attributed to a masking of the effect by other factors such as adsorption phenomenon and the imprecision of analytical data near detection limits. No consistent enhanced or adverse effects of humic acid were observed for concentrations using the two different type reverse osmosis membranes.

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SECTION 3

RECOMMENDATIONS

It is recommended that the FT-30 membrane be used in future concentration studies because of better solute rejection, recovery, and chemical resistance as compared to the cellulose acetate membrane previously employed. Short-term exposure ($\sim$ 7 days) to normal chlorine disinfection levels did not change the apparent rejection properties of the membrane. Further studies are needed to fully define the generation of low level contaminants with oxidative disinfectant exposure.

It is recommended that steps be taken to satisfy adsorptive demands during sample collections using the reverse osmosis concentration method. Preconditioning of this nature could involve exposing the membranes and other system components to waters (both at ambient and concentrated levels) being sampled. This type treatment should help maximize recovery of organics in any stream where significant adsorption may occur.

It is recommended that the apparent losses to adsorption be investigated in further detail under conditions more favorable to analytical chemistry. By removing some of the major analytical complications (i.e., mixed salts, acetone, and humic acid) and spiking at higher solute levels, better accuracy will be provided. Extended test periods and expanded sampling schedules should be instituted to better determine the attainment of steady-state conditions and characterize the solute sorption phenomena. It is expected that more benefit will be gained from these modifications than will be lost in deviating from "real world" modeling. Answers to these questions should be sought:

1. Is the adsorption phenomenon associated with the membrane or other system components?
2. Is the phenomenon reversible?
3. Can the "demand" for solute be satisfied?
4. Is the adsorption a function of the solute concentration?

It is also recommended that the search continue for a better anion exchange membrane. This membrane is needed whenever concentration procedures require the concurrent removal of inorganic burden. Research is being conducted to develop improved membranes with polyolefin backbone structures in the laboratories of several major membrane manufacturers. These membranes should possess better chemical resistance than the styrene/divinylbenzene based membranes currently in production. The apparent chlorine sensitivity of the MA 3475 membrane indicates manufacturers' claims may be adequate for electrodialysis applications, but are less than optimum for organic sampling.

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SECTION 4

EXPERIMENTAL PROCEDURES

The description of experimental procedures is divided into two major sections, membrane testing and analytical chemistry. The two subject elements are discussed separately, and the removal of analytical chemistry details from the discussion of the membrane evaluation should facilitate understanding of the materials.

A. MEMBRANE TESTING

1. Background

Drinking water contamination of both ground and surface water sources is an area of general public concern. Some contamination problems are acute and readily identifiable in a biological or chemical form (e.g., giardia cyst, hepatitis and poliomyelitis virus, lead and nitrate) (1-4). Pollution problems of this nature can be addressed with current treatment technologies such as disinfection or ion exchange. In other circumstances, for instance benzene, trichloroethylene, or methylchloroform contamination, the undesirable constituent may be easily identified, but the water source may have to be abandoned because viable, economically feasible treatment technologies are not available (5).

Readily identifiable acute toxicants, if present, usually represent a very small fraction of the material present in most drinking waters. There remains a significant amount of substances that cannot be analyzed due to the complex nature of the compounds, inadequate methodologies, interference from matrix effects, or other factors. To date, the best methods to determine whether this unidentified group of compounds represents a significant potential health problem have centered around toxicity evaluations of drinking water concentrates with biological assessments such as the Ames bacterial mutagenicity test (6,7) and the more classical rodent bioassay studies (8). New in vitro assays are also under investigation in an effort to find faster, more economical and sensitive methods to assess the health risks associated with trace organic contaminants in potable water. However, all of these tests require some concentration of sample. Several methods have been evaluated for the preparation of drinking water concentrates to be used for health effects testing. Some of these concentration/isolation methods include reverse osmosis concentration, adsorbent resin concentration/isolation, lyophilization concentration, liquid-liquid extraction, and supercritical fluid extraction.

The EPA has established an on-going program in drinking water research. Resulting toxicological data demonstrates the presence of mutagenic constituents in samples of concentrated, recycled water (9,10). Chemical analysis of these source waters has revealed the presence of known

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carcinogens (11). The toxicological examination of concentrates suggests that carcinogenic activity in drinking water samples is not confined to the volatile or gas chromatographable substances.

Over the last eight years EPA has primarily utilized two concentration/isolation techniques for preparation of drinking water concentrates to use in health effects testing. The first method is a concentration based upon the use of adsorbent resins (XADs) to trap and recover organic materials from water. The second method takes advantage of the selective permeation properties of reverse osmosis (RO) membranes to concentrate organic substances dissolved in water. The primary objective of either method is the same: the enrichment and/or recovery of organic substances usually present at trace levels in water.

Ideally, the concentration step should yield a representative fraction of the solutes without altering or destroying the chemical species present. Optimally, the concentration method should yield a quantitative recovery of the solutes. In collaboration with EPA, Gulf South Research Institute has developed a scheme for the concentration, separation, and recovery of organics based on reverse osmosis membrane separations. In this scheme, there are multiple process steps to separate organic and inorganic materials. Ideally, the most representative sample is an aqueous concentrate that can be used directly in toxicological tests. GSRI demonstrated the feasibility of using reverse osmosis concentration and Donnan dialysis control of organics in an evaluation of toxic effects of organic contaminants in recycled waste water (12). Reverse osmosis procedures have been developed and refined over the last eight years under the auspices and financial support of the EPA. The procedures were orginally designed for use in conjunction with solvent extraction to generate substantial quantities of highly concentrated organics for toxicological and analytical evaluation. In the earlier studies, cellulose acetate was selected as the primary reverse osmosis membrane because of its commercial availability, chlorine resistance, and salt rejection. The same basic sample collection procedure was maintained in later studies so that results would be comparable.

Essential components of the concentrator are illustrated in Figure 1. Water to be concentrated is circulated through the concentrate compartment while hydraulic pressure is maintained higher than the osmotic pressure. The concentrate is generated by the removal of RO filtered water from the system via the permeate flow. Reverse osmosis offers the following advantages for concentration of organics in water for analysis and assessment of health effects.

1. A sample can be concentrated without removing the solutes from the aqueous matrix.
2. No phase changes are required.
3. It is a relatively low-temperature process.
4. Large volumes can be processed.
5. High concentration factors can be achieved.
6. The system has been demonstrated in the field.
7. A broad spectrum of organics is recovered.

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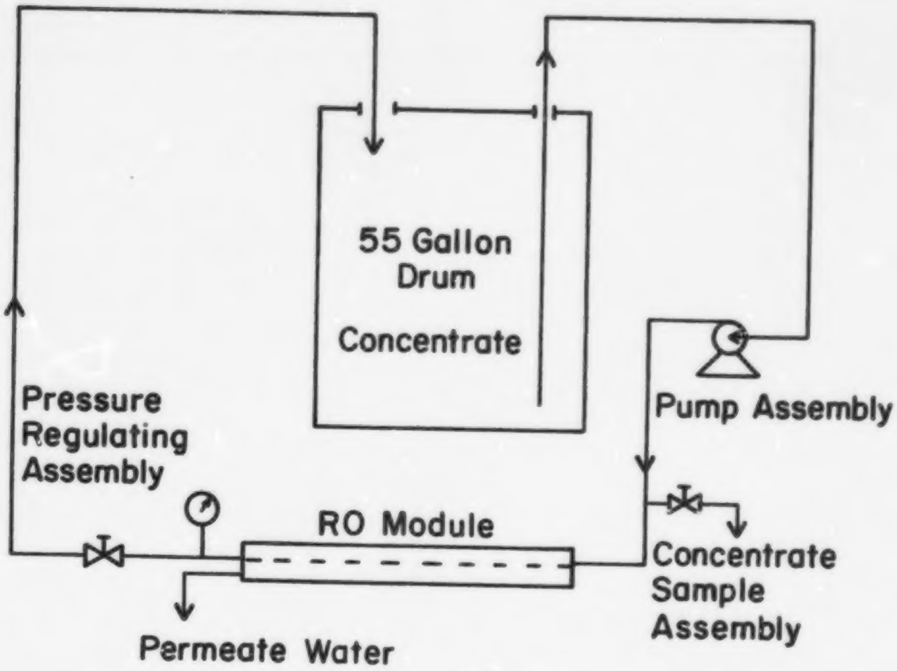
55 Gallon Drum
Concentrate
Pump Assembly
Pressure Regulating Assembly
RO Module
Concentrate Sample Assembly
Permeate Water

Figure 1. Essential elements of a reverse osmosis (RO) concentrator.

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8. Inorganic ions can be removed concurrently with organic concentration when complete Donnan deionization is performed.

2. General Test Procedures

The two basic types of membranes evaluated in this study were reverse osmosis and Donnan membranes. RO membranes (the essential organic rejecting or concentrating membrane) are typically prepared from synthetic polymers such as cellulose acetate (CA), polyamide, or composite materials and are used commercially to desalinate brackish or sea water. The Donnan membranes (used to control the buildup of inorganic species as organic concentration occurs) are also prepared from synthetic polymers, but possess one major characteristic that readily distinguishes them from RO membranes: Donnan membranes have chemically charged sites throughout the basic polymer material. These sites may be either positively or negatively charged depending upon the chemical moiety attached to the basic polymer structure. This property allows dissolved charged species such as dissociated inorganic salts to move across the membrane by hopping from site to site. Thus, ions on one side of the membrane can be exchanged for similarly charged ions on the other side. For this reason, Donnan membranes are often referred to as ion exchange membranes. Membranes with fixed positive charges (which allows the movement of negatively charged ions) are termed anion exchange membranes. Negatively charged membranes are termed cation exchangers.

Three stages of membrane evaluations were completed in this study: a) preliminary membrane screening, b) secondary membrane screening, and c) concentration tests.

a. Preliminary Membrane Screening--

The first level of evaluation, preliminary screening, provided initial program optimization by selection and development of only the most promising commercially available membranes. The preliminary screening ranged from a critical review of the performance and operating specifications for the RO membranes to actual laboratory tests. Four membranes, two RO and two Donnan, were selected for continued evaluation in the secondary screening phase. Details of the preliminary screening procedures and criteria applied for membrane selection are presented in Sections 4.A.4 and 4.A.5. of this report.

b. Secondary Membrane Screening--

The second stage of membrane evaluation was conducted on the cellulose acetate and thin film composite (FT-30) reverse osmosis membranes, as well as the Nafion^{R} cation exchange and MA 3475 anion exchange Donnan membranes. All secondary membrane screenings were conducted by using the test assembly shown in Figure 2. This equipment represents a more sophisticated version of the basic RO concentrator illustrated earlier in Figure 1, and includes a Donnan membrane loop in addition to the RO loop. This equipment (Figure 2) and its use and operation are discussed more fully in Sections 4.A.3 and 4.A.7.

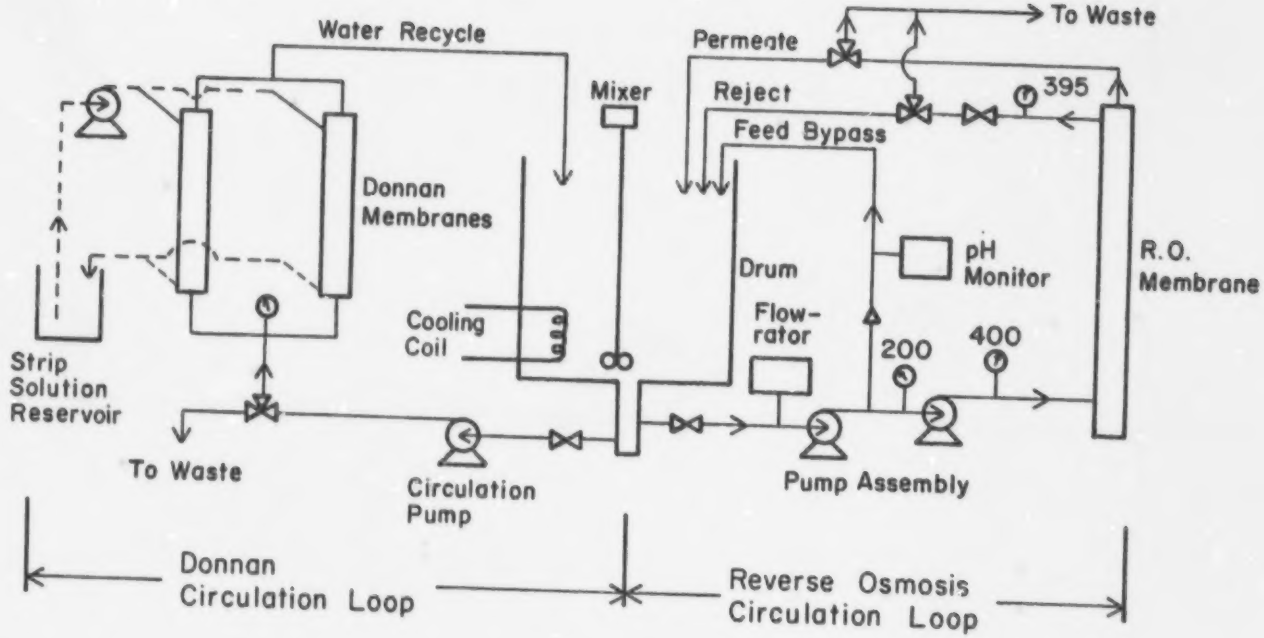
Water Recycle
Mixer
Permeate
Reject
Feed Bypass
To Waste
395
Donnan Membranes
Drum
pH Monitor
R.O. Membrane
Cooling Coil
Flow-rator
200
400
Strip Solution Reservoir
To Waste
Circulation Pump
Pump Assembly
Donnan Circulation Loop
Reverse Osmosis Circulation Loop

Figure 2. Major components of a reverse osmosis (RO) concentration/Donnan dialysis organic recovery system.

The secondary screening experiments were conducted with several specific objectives. The leachable organics were examined by recirculating organic free water (OFW) through the membrane recirculation loop of interest and analyzing the recirculating water at the beginning and end of the recirculation period. Another series of tests was run with chlorine in the OFW to determine what types of leachable products are encountered in the presence of chlorine. Organic chemical losses due to adsorption and volatility were estimated from data generated in tests where the level of selected model organics was monitored as a function of total recirculation time in the system. The same series of tests was also designed to yield information on the rejection of model solutes by RO membranes and losses of solutes through the Donnan membranes. The effect of humic acid on the membrane/organic solute behavior was evaluated by adding humic acid to the test water and reevaluating solute retention by the membrane.

A three-stage screening protocol was developed to evaluate the RO and Donnan membranes during secondary screening tests. The protocol was designed to be responsive to stated objectives. The three stages were *flushing*, *system blank determination*, and *membrane solute screening*. The stages used and sampling regimes assigned for each test were determined by its objectives. For example, a series of samples were collected during the flush stage if the experimental objective was to determine the effectiveness of flushing. If the experimental objective was to evaluate what organics would be leached from the membranes, samples were collected at the beginning and end of the system blank stage, and the run would be terminated at that point. No actual concentrations were performed in the secondary screening tests since permeate streams were returned to the concentrate drum.

The basic three-stage protocol (flush, system blank, and solute screening), is incorporated and described in the standard operating procedures (SOPs) for the RO and Donnan evaluations. Both membrane test protocols are included as Appendices A and B, respectively. Both SOPs include the same three basic stages, but slight variations between A and B are incorporated to accommodate differences in the two membrane types. Simply stated, Donnan membranes require the use of chemical "pump" or "strip" solutions while RO membranes have permeate streams.

The first phase (flush) of the basic test protocol provided a well-defined flush regime with OFW to start each membrane evaluation run. Flushing basically involved repetitive rinses with OFW to remove residues from manufacture or earlier tests. The flush regimes detailed in the SOPs of Appendices A and B were used throughout the study.

A set volume of organic-free water (OFW) was added to the process reservoir after the "flush" regime was completed. The OFW was recirculated through either the RO or Donnan loop depending upon which membrane was being evaluated. The "system blank" phase of the test SOP was performed to determine the leachables and establish a baseline organic composition prior to spiking the water with organic solutes. Samples of the test water were collected at the beginning and end of the recirculation period (4 hr for RO and 3 hr for Donnan membranes) for the "system blank" phase of the test SOP.

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The last stage of the basic test protocol, "solute screening," was initiated by spiking the OFW with model organic solutes. Three samples were collected during the "solute screening" phase. The recirculating water was sampled near the beginning and at the end of a 4 hr period of total recirculation (both permeate and reject flows returned to the process reservoir) to allow calculation of solute losses to the environment (volatilization) and system components (adsorption). A third sample, taken from the permeate stream, was collected at the same time as the second reservoir sample for the RO membrane evaluations. Membrane solute rejections were calculated from the solute concentrations in the feed/permeate pair of samples collected at the end of the 4 hr period.

For evaluation of the Donnan membranes, two reservoir samples were collected as in the RO membrane test. These samples provided estimates of organic losses from the system. Since very little water is transported across the Donnan membranes, a permeate sample is not relevant in their testing. Instead, the Donnan membranes were dialyzed against a salt solution, and this "strip" or "pump" solution was sampled at the same time as the last sample from the process reservoir. This allows estimation of the amount of solute lost to the chemical "pump" solution.

A variety of analytical measurements and procedures was used to analyze the levels of various organic solutes. These methods included GC/MS, gas chromatography with flame ionization detection (GC/FID), gas chromatography with electron capture detection (GC/ECD), high performance liquid chromatography (HPLC), and radioactive scintillation counting. All the specific analytical methods are discussed in Section 4.B and Appendices G through N. Further details on the test equipment are given in Section 4.A.3, and test procedure details are provided in Section 4.A.7, and Appendices A and B.

c. Concentration Test--

Concentration tests were performed on the two best RO membranes and the Donnan cation exchange membrane. In this series of tests, model solute recovery efficiencies for the combined RO concentration and Donnan cation exchange components were evaluated. The recovery of model organic solutes was determined while undertaking 50-fold volumetric concentrations. A diagram illustrating the concentration scheme (volumetric reduction) used to reduce 500 liters to 10 liters is shown in Figure 3. The 500 liter (132 gallon) initial sample volume was concentrated in three portions of 167 liters (44 gallons) each using existing scale processing equipment (see Figure 2). Organic recoveries and losses were estimated from concentrations of solutes measured in samples taken from various streams at increasing stages of concentration. Section 4.A.8 provides further details on test methods, equipment used, and results of these tests.

3. Materials, Reagents, and Test Equipment

Analytical model solute reagents used in this study are listed in Table 1. The list is sectioned into the model organic solutes used in developing analytical methodologies and challenging the membranes evaluated here. The other section details chemicals used to prepare the inorganic matrix for the test water, chemicals used as strip solutions, for pH con-

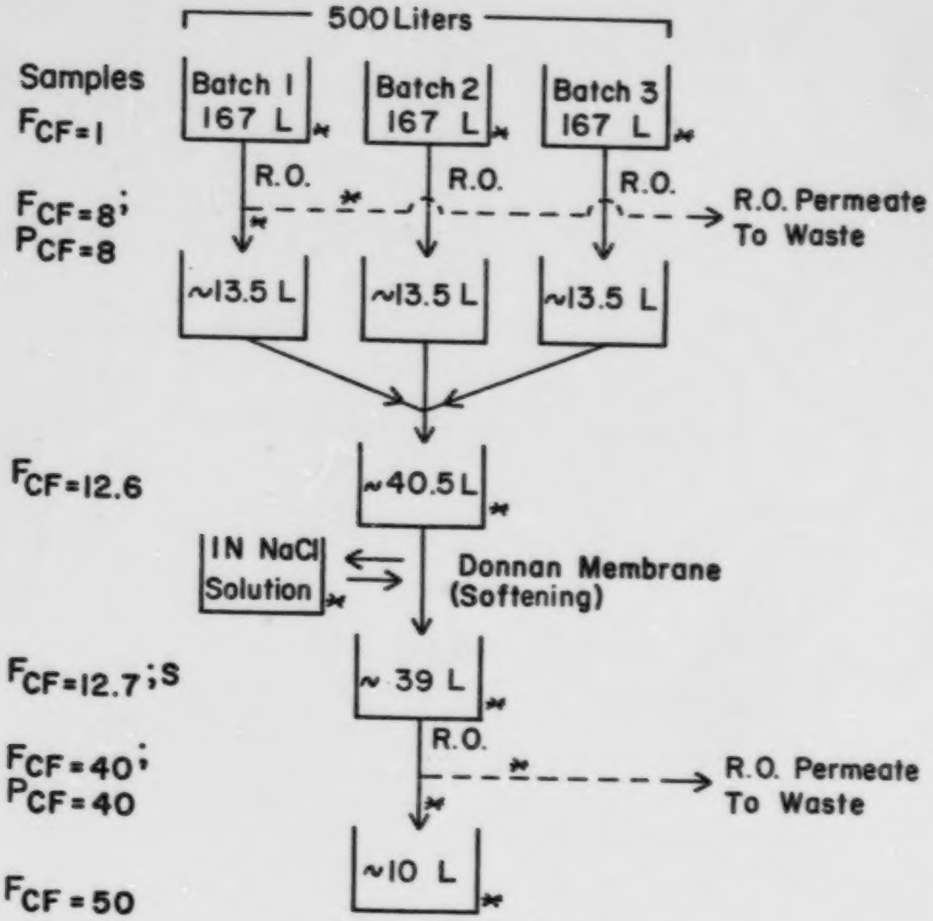
500 Liters
Samples
$F_{CF=1}$
Batch 1 167 L
Batch 2 167 L
Batch 3 167 L
R.O.
R.O.
R.O.
$F_{CF=8}$;
$P_{CF=8}$
R.O. Permeate To Waste
~13.5 L
~13.5 L
~13.5 L
$F_{CF=12.6}$
~40.5 L
1N NaCl Solution
Donnan Membrane (Softening)
$F_{CF=12.7}$;S
~39 L
R.O.
$F_{CF=40}$;
$P_{CF=40}$
R.O. Permeate To Waste
~10 L
$F_{CF=50}$
*

Figure 3. General experimental design and sampling regime * for the reverse osmosis concentration runs.

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TABLE 1. MATERIALS AND REAGENT LIST

Reagent	Supplier	Grade or Purity
Acetone	J.T. Baker Chemical Co.	"Baker Analyzed" Reagent
Anthraquinone	Aldrich	97%
Benzo(e)pyrene	Aldrich	99%
Biphenyl	Aldrich	unknown
Bis(2-ethylhexyl)-phthalate	Chem. Service	95 + %
Caffeine	Aldrich	unknown
Calcium chloride	Matheson, Coleman & Bell	Reagent, A.C.S.
1-chlorododecane	Aldrich	unknown
Chloroform	Aldrich	99 + %
5-Chlorouracil	Aldrich	99%
Crotonaldehyde	Aldrich	85% + 15% H_2O
2,4'-Dichlorbiphenyl	Analab	99%
2,4-Dichlorphenol	Aldrich	99%
2,6-Di-tert-butyl-4-methylphenol	Aldrich	99%
Furfural	Aldrich	99%
Glucose	Aldrich	unknown
Glycine	Aldrich	98%
Humic acid	EPA	--
Isophorone	Aldrich	99%
Methyl isobutyl ketone	Aldrich	99.5%
Quinaldic acid	Aldrich	99%
Quinoline	Aldrich	96%
Sodium bicarbonate	J.T. Baker Chemical Co.	"Baker Analyzed" Reagent
Sodium chloride	Mallinckrodt	Analytical Reagent
Sodium hydroxide	J.T. Baker Chemical Co.	"Baker Analyzed" Reagent
Sodium hypochlorite	J.T. Baker Chemical Co.	"Baker Analyzed" Reagent
Stearic acid	Sigma	99%
Sodium sulfate (anhydrous)	Mallinckrodt	Analytical Reagent
2,2',5,5'-Tetra-chlorobiphenyl	Analab	99%
Trimesic acid	Aldrich	97 + %
Water	See Section 4.A.3d	

trol, and to prepare the chlorine exposure solutions.

Two sets of test apparatus were used to evaluate membranes during this program. The first apparatus was used for the evaluation of Donnan anion exchange membranes during the preliminary screening. The second test apparatus was used for both the secondary screening and the subsequent concentration runs. A third piece of equipment was used for the production of organic free water. The OFW was required to flush the membrane system and to prepare test waters.

a. Donnan Dialysis Test Apparatus Used for Preliminary Screening--

Figure 4 shows basic components of the test apparatus used for preliminary screening of anion exchange membranes. The dialysis cell used to conduct these tests provided an active membrane area of 53 cm^2. The concentrate reservoir was charged with one liter of solution and was dialyzed against a sodium hydroxide pump solution (0.5M). Performance of the various test membranes were monitored by analyzing the concentration of anions in the concentrate bath reservoir. Further detail on the test procedures and test results are offered in section 4.A.5a.

The Nafion^{R} cation exchange membrane was tested using the concentration scale equipment illustrated earlier in Figure 2. Procedures followed in these tests are also discussed in Section 4.A.5a.

b. Test Apparatus for Secondary Screening of Donnan and RO Membranes--

Secondary membrane screening studies were performed using concentration scale (~200 liter unit capacity) equipment and commercially available Donnan and RO membranes. The equipment illustrated earlier in Figure 2 was utilized in these screenings. Tests on the RO membranes required blocking the Donnan components, shown on the left half of the figure, by proper valve selection and installing either the cellulose acetate or FT-30 membrane into the RO recirculation loop. The pH of the concentrate solution was maintained by the addition of 0.2M HCl with a metering pump controlled by the pH monitor/controller. Details of procedures are offered in section 4.A.7 and Appendix A.

In secondary screening tests to evaluate the Donnan membranes, the components shown on the left half of Figure 2 were utilized. RO equipment on the right half of the illustration was shut off. Depending upon which membrane was to be evaluated, either the Nafion^{R} cation exchange or Ionac MA 3475 anion exchange membrane was installed. All secondary screening tests were performed with total recycle systems and no overall concentration. Details of procedures are provided later in section 4.A.7 and Appendix B.

c. Reverse Osmosis Concentration Test Equipment--

The same equipment used to conduct secondary membrane screenings was used to perform the membrane concentration test. Details of the procedures followed in the concentration runs are provided in Section 4.A.8 and Appendix F. A 500 liter (132 gallon) initial sample volume was processed in three equal batches of 167 liters (44 gallons) each. Both the reverse osmosis circulation loop and the Donnan circulation loop were utilized in these tests although not at the same time. The RO permeate was discarded

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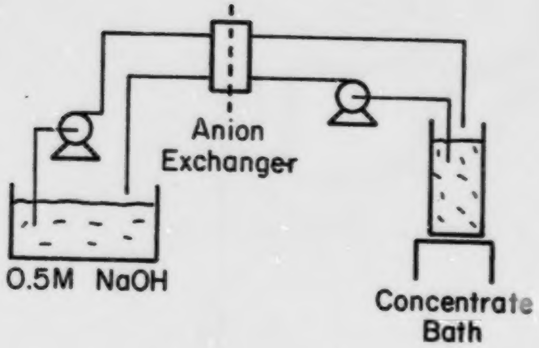
Anion Exchanger
0.5M NaOH
Concentrate Bath

Figure 4. Simplified drawing of a Donnan dialysis test apparatus.

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in the concentration test runs, rather than recycling as in the secondary screening.

d. Organic Free Water Production Equipment--
A system for producing OFW was constructed and operated over 100 hours while debugging and product water characterization were completed. Estimates of OFW quantities required for the study indicated that as much as 1140 liters (300 gallons) a week were needed. Based on these estimates, an intermediate sized multitreatment system was assembled and automated to produce OFW for the project.

The multi-component water treatment process included carbon filtration with approximately 1 kilogram of Cullar Type D carbon (Culligan Corp.). The carbon-filtered water was filtered through a 5 µm particulate filter (Hytrex model 6x-5-9) and then reprocessed through a small (10 gallons per hour) Film Tec FT-30 reverse osmosis membrane filter. The treatment system's finished water was filtered through a submicron final state filter (Gelman Preflow 100 filter) before delivery to the collection reservoirs. The system's product water was accumulated in two 55 gallon stainless steel drums. The filling was automated with level controls in the collection drums to allow unattended operation throughout the night. The OFW production system allowed complete replenishment of water reserves during overnight operation.

4. Selection of Study Membranes for Evaluation

An initial membrane survey based on anticipated operating criteria and commercial availability was completed prior to selection of membranes for laboratory evaluation. After the initial survey, two RO membranes (Osmonics cellulose acetate and Film Tec FT-30 composite) and five Donnan membranes (Ionac MA 3475, RAI 4025, RAI 4035, RAI 5025, and RAI 5035) were chosen for evaluation in laboratory screening tests. The two RO membranes, the Dupont Nafion^R membrane (cation exchange) and the Ionac MA 3475 membrane (anion exchange), were selected for characterization in the secondary membrane screening test.

Information on commercially available RO membranes was solicited from the suppliers listed in Table 2. Product information was screened to locate RO membrane types that might offer improved rejection of organic solutes and to assess the chemical compatibility of these membrane materials. RO membranes were considered for laboratory evaluation if 1) they were commercially available, 2) they offered potential for generally improved organic solute recovery, and 3) they possessed the required chemical stability characteristics.

The RO membranes utilized in this study had to meet certain chemical compatability criteria. As in the case of the Donnan membranes, the basis for these criteria comprised operating conditions that the membranes would be subjected to during field sampling of organics. The primary criteria were that 1) the membranes must be able to operate at normal design pH (approximately 5) and 2) the membranes must be able to tolerate a low to moderate free chlorine residual (<5 mg/L). The pH requirement was not difficult to meet, but the chlorine exposure requirement presented a formidable problem for many commercially available RO membranes.

TABLE 2. AVAILABILITY OF REVERSE OSMOSIS MEMBRANES PRODUCED COMMERCIALLY BY VARIOUS U.S. MANUFACTURERS

Manufacturer/source	Production membranes	Type
Puretech, Inc.	yes	cellulose acetate blend
Osmonics, Inc.	yes	cellulose acetate (polyethyleneimine polyamide composite polyvinylidinefluoride)
Desalination Systems, Inc.	yes	cellulose acetate polyamide composite
T.J. Engineering, Inc. (Osmonics)	yes	cellulose acetate
Envirogenics Systems Company	yes	cellulose acetate blend
Dow Chemical Company	yes	cellulose triacetate
Dupont	yes	polyamide
El Paso Environmental Systems	yes	cellulose acetate
UOP*	yes	cellulose acetate
Film Tec†	yes	polyamide composite polysulfone thin-film composite

*UOP is currently developing several membranes that may be considered in future programs.

†Film Tec discusses the composition of their membrane in Department of the Interior Report No. 14-34-0001-0443.

Table 3 lists the critical chemical stability properties of cellulose acetate and other more recently developed polymeric RO membrane materials which are available commercially. It is evident from the pH data that many of the RO membranes would be acceptable for further study. However, examination of the chlorine tolerance data indicates only two readily available RO membranes, cellulose acetate and FT-30, with any chlorine tolerance. All reported pH and chlorine values represent averages of quoted literature values. The actual numbers from each manufacturer/supplier may differ and reflect slight differences in membrane composition and/or the subjective judgement of the manufacturers. The other membranes are apparently quite susceptible to degradation by chlorine levels typical of those used in this study, and those expected to be encountered in actual field sample collections. The cellulose acetate and FT-30 RO membranes were selected for evaluation in laboratory tests primarily on the basis of their chlorine tolerance and difference in spectrum of expected organic solute rejections.

RO membranes made from cellulose acetate were included in the study because they met the general chemical compatability requirements and because they have been used in all earlier field concentrations. Considerable benefits will be realized by having basic organic solute rejection data on the cellulose acetate membrane to establish a reference point with which the newer improved membranes can be compared.

TABLE 3. STABILITY PROPERTIES OF VARIOUS COMMERCIALLY AVAILABLE RO MEMBRANES

Membrane type	Salt rejection	Acceptable pH range	Chlorine tolerance
cellulose acetate	>97-99	2-8 intermittent 3-7 continuous	≤1 continuous ≤5 intermittent
polyethyleneimine (PEI)	99	4.5-11	oxidation sensitive
polyamide (PA)	99	5-12	oxidation sensitive
polyvinylidinefluoride (PVF)	99	0.5-10.5	oxidation sensitive
*polybenzimidazole (PBIL)	99	1-12	resistant
FT-30 (polysulfone thin-film composite)	97-99	3-11	short term resistance

*produced by Teijin, Limited, of Tokyo, Japan, but not available in the United States

Many domestic suppliers offer cellulose acetate based membranes. Cellulose acetates from different suppliers can differ in acetyl content. Various suppliers offer membranes produced from cellulose diacetate, cellulose triacetate, and blends of di- and triacetates. Much of the basic compositional data on commercial membranes is proprietary and could not be obtained. However, the organic solute rejection of membranes formulated from varying cellulose acetate compositions would not be expected to differ significantly. Therefore, project resources were better utilized by evaluating a single cellulose acetate membrane from a reliable commercial source and directing attention to the newer improved RO membranes.

Table 4 lists the suppliers of Donnan membranes that were contacted. These suppliers represent manufacturers who are or have been in the business of producing or using commercial ion exchange membranes. Membrane samples and product literature were requested from each of the suppliers offering membrane production.

Table 5 lists pH and chlorine tolerance information on the Dupont Nafion^{R} cation exchange membrane and the anion exchange membranes that were available commercially. Anticipated operating conditions served as the basis for determining selection criteria. The cation exchange membranes may be routinely subjected to 0.5 to 1.0 M HCl when operated in the deionization mode. The anion exchange membranes can be exposed to 0.5 to 1.0 M NaOH in this mode. In addition, membranes may occasionally be exposed to free chlorine residuals of 1-5 mg/L. Matching these criteria against the performance criteria listed in Table 5 shows that only the Nafion^{R} cation

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exchange membrane and five of the anion exchange membranes have potential applicability.

TABLE 4. AVAILABILITY OF ANION EXCHANGE MEMBRANES PRODUCED COMMERCIALLY BY VARIOUS U.S. MANUFACTURERS

Manufacturer	Production membranes	Type
Ionac Chemical Company	Ionac MA 3475	Quaternized styrene divinylbenzene polymer (fabric reinforced)
	Ionac MA 3148	Quaternized styrene divinylbenzene polymer (fabric reinforced)
RAI Research Corporation	R4025	Quaternized pyridine grafted FEP Teflon
	R5025	Quaternized pyridine grafted polyethylene
	R5035	Quaternized vinyl benzylamine grafted polyethylene
	R4035	Quaternized benzylamine grafted FEP Teflon
Ionics, Incorporated	103-QZL-386	Quaternized vinyl copolymers (fabric reinforced)
	103-PZL-386	Quaternized vinyl copolymers (fabric reinforced)
AMF	no production	
Union Carbide	no production	
Rohm & Haas/Romicon	no production	
Diamond Alkali	no production	
Dow Chemical	no production	

Table 6 details sources and available manufacturer specifications for the membranes selected for laboratory evaluation in this study.

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TABLE 5. STABILITY PROPERTIES OF VARIOUS COMMERCIALLY AVAILABLE DONNAN MEMBRANES

Membrane type	Acceptable pH range	Chlorine tolerance
Dupont Nafion^{R}	excellent	excellent
Ionac MA 3475	>10 M	≤150 mg/L
Ionac MA 3148	NR*	NR*
RAI R4025	excellent	excellent
RAI R5025	excellent	excellent
RAI R5035	excellent	excellent
RAI R4035	excellent	excellent
Ionics 103-QZL-386	<9	NR*
Ionics 103-PZL-386	<9	NR*

*NR - Not recommended

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TABLE 6. MANUFACTURERS, SUPPLIERS, AND PERFORMANCE SPECIFICATIONS (WHERE AVAILABLE AND RELATED TO STUDY) FOR MEMBRANES EVALUATED IN LABORATORY TESTS

Membrane	Data	Specifications	Observed performance
cellulose acetate	manufacturer	Osmonics, Inc.	--
	model	OSMO-112-97-CA	--
	salt rejection	94-97%	97%
	feed concentration	1,000 ppm NaCl	500 ppm (mixed salts)
	pressure	400 psig	400 psig
	module flux	0.38 1/min	0.38 1.min
	temperature	25°C	26°C
	percent conversion	10%	4%
FT-30	manufacturer	Film Tec Corporation	--
	model	BW30-20-26	--
	salt rejection	>95%	99%
	feed concentration	10,000 ppm NaCl	500 ppm (mixed salts)
	pressure	350 psig	400 psig
	module flux	0.38 1/min	0.94 1/min
	temperature	25°C	26°C
	percent conversion	5%	4%
Nafion^R	manufacturer	Dupont	--
	supplier	Perma Pure Products	--
	model	PD-750-72P	--
MA 3475	manufacturer	Ionac Chemical Co.	--

5. Preliminary Membrane Screening

Preliminary membrane screening criteria were applied and tests were conducted to determine the most promising membranes to carry forward to the secondary membrane screening phase. The preliminary screening was used to maximize the productivity of the more detailed and costly test evaluations to follow. The preliminary tests, their results, and selection criteria are discussed below. The discussion is divided by membrane type - a) Donnan membranes and b) RO membranes.

a. Donnan Membranes--

The primary function of the Donnan membranes in the overall organic concentration/recovery process was to reduce the inorganic salt precipitation potential of the aqueous concentrate. The cation exchanger provides exchange of positively charged ions, and the anion exchanger replaces the negative ions. The organic concentration process benefits in several ways from the efficient operation of the Donnan deionization system. One benefit is the minimization of precipitation of low solubility inorganic salts (e.g., $CaSO_4$, $CaCO_3$) and the undesirable potential of surface adsorption of organics on these precipitates. Also, membrane scaling and fouling are reduced and higher water fluxes are realized.

For the Donnan deionization to perform at maximum efficiency, cations in the concentrate must be exchanged with "pump" solution cations without any accompanying transport of anions across the cation exchange membrane. Similarly, only anions should move across the anion exchange membrane. Figure 5 illustrates an anion exchange membrane and initial test conditions of an experiment to determine the rate of efficient anion exchange from a concentrate solution into a pump solution bath. The driving force for the process is the large hydroxide ion gradient across the membrane.

In principle, the charged nature of the membrane should prevent the movement of co-ions (those with the same charge as the membrane) across the membrane. Unfortunately, the "perfect" membrane has yet to be produced and some co-ions do move across due to imperfections. In good membranes with high permselectivity, the rate of noneffective transport (so termed because the charge of the "pump" ion is balanced by the co-ion transport rather than by the desired coupled movement of ions from the opposite side of the membrane) is one to three orders of magnitude less than the desired removal of ions from the concentrate bath.

The effective removal rate of ions was determined in preliminary membrane screening tests. Figure 5 represents the initial conditions in such a pumping rate test. Figure 6 illustrates the concentrate solution's anion decay rate experienced for chloride ion in a pump rate test. The pumping rate for a membrane is determined from the slope of its decay curve. Table 7 lists pumping rates that were calculated from ion decay curves of the anion exchange membranes chosen for preliminary laboratory screening. The pumping rate is expressed in moles of the ion being pumped (concentration x bath volume) per second and is normalized for the membrane area. The pumping rates listed in Table 7 are shown graphically in Figure 7.

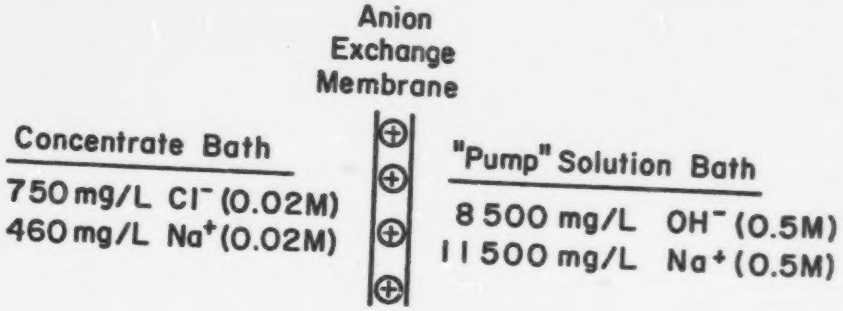
Anion Exchange Membrane
Concentrate Bath
750 mg/L Cl⁻ (0.02M)
460 mg/L Na⁺ (0.02M)
"Pump" Solution Bath
8 500 mg/L OH⁻ (0.5M)
11 500 mg/L Na⁺ (0.5M)

Figure 5. Anion exchange membrane and initial experimental conditions for "pumping" rate test.

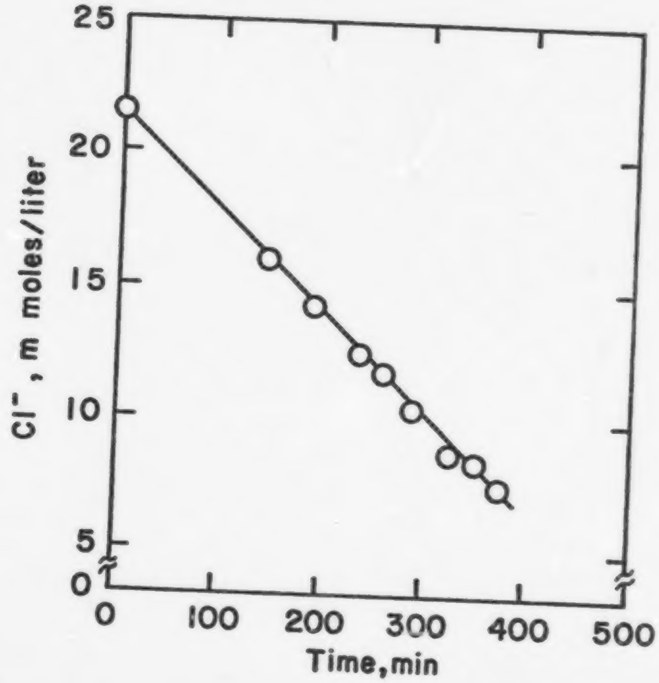

Figure 6. Concentrate bath ion decay curve using Ionac MA 3475 anion exchange membrane (53 cm^2).

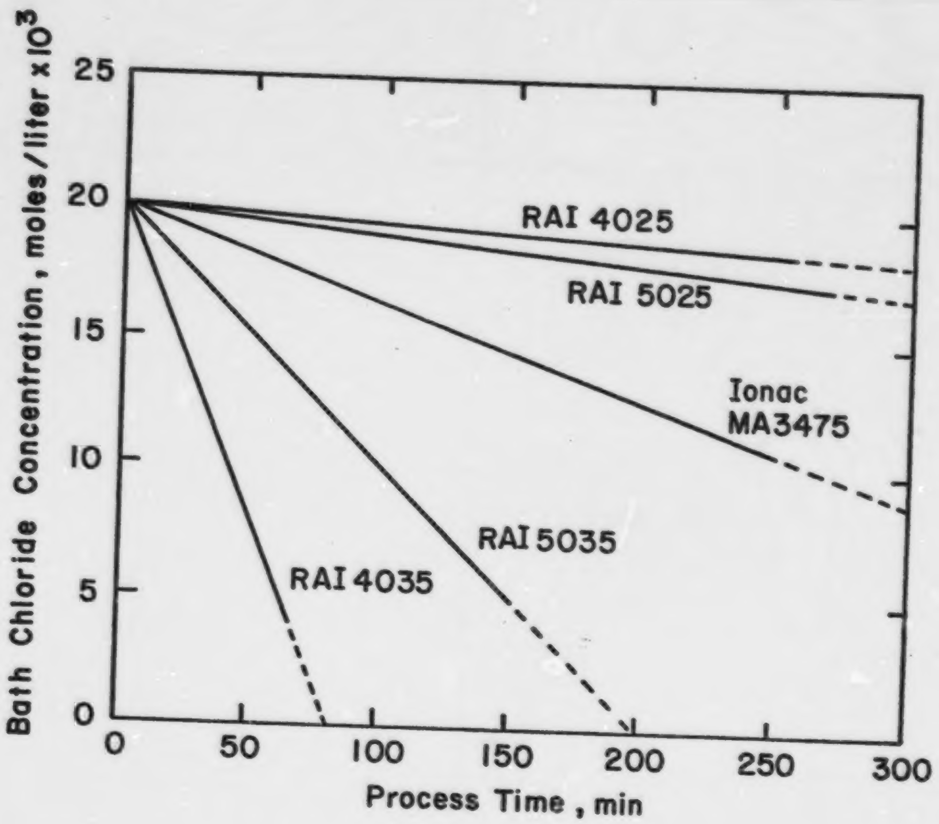

Figure 7. "Pumping" rates for various anion exchange membranes (1 liter reservoir, 53 cm^2 membrane area).

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TABLE 7. PUMPING RATES, LEAKAGE RATES, AND EFFICIENCIES FOR VARIOUS ANION EXCHANGE MEMBRANES

Membrane	Pumping rate moles/cm^2-sec	Leakage rate moles/cm^2-sec	Efficiency*
Ionac MA3475	1.0×10^{-8}	1.5×10^{-11}	667
RAI 4025	1.7×10^{-9}	8.1×10^{-12}	210
RAI 4035	7.4×10^{-8}	1.1×10^{-9}	67
RAI 5025	2.9×10^{-9}	$<10^{-10}$	>29
RAI 5035	4.9×10^{-8}	9.8×10^{-10}	50

*Efficiency - pumping rate/leakage rate

The noneffective transport rate for the anion exchange membranes tested was termed "leakage" rate. The leakage rate was determined in a manner similar to the pumping rate determination. Figure 8 illustrates the initial test conditions for an evaluation of leakage rate. In this determination, the rate of increase of ions in the concentrate solution is established under conditions where, theoretically, there should be little or no ion transport across the membrane. Figure 9 reflects such an increase of ionic content in the concentrate bath. The slope of this line is an indication of the rate of noneffective transport through imperfections in the membrane. The initial portion of the curve usually represents a membrane conditioning period and is not a factor in the leakage rate calculation. Table 7 lists leakage rates for the Donnan anion membranes tested. Leakage rate values were determined from the slope in a manner similar to that used to calculate the pumping rates.

Final selection of an anion exchange Donnan membrane for testing in the secondary screening studies was based upon the efficiency of the membrane. The membrane efficiency was defined as the ratio of the pumping rate to the leakage rate. Table 7 lists efficiencies of the five anion exchange membranes evaluated in preliminary screening test. The Ionac MA 3475 membrane exhibited 6 times the efficiency of the next closest competitor, RAI 4025, and approximately 10 times the overall pumping rate of the RAI 4025 anion exchange membrane. The Ionac MA 3475 membrane was advanced to the secondary screening test phase based upon the above efficiency and rate data.

Previous EPA field concentrations using the reverse osmosis concentration method (EPA Contract Nos. 68-03-2464, 68-03-2367, 68-03-2713, and 68-03-2550) have utilized the Nafion^R cation exchange membrane along with the cellulose acetate reverse osmosis membranes to achieve concentrations in excess of 50X while generally eliminating or minimizing inorganic solids precipitation. These concentrations were completed using the Nafion^R membrane component to soften the concentrate water (i.e., using Na$^+$ to

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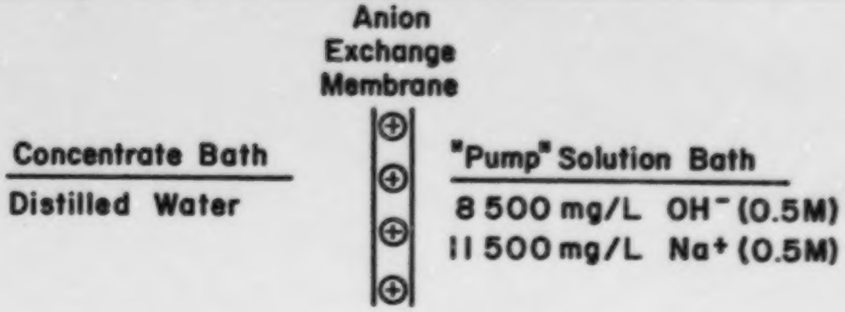
Anion Exchange Membrane
Concentrate Bath
Distilled Water
"Pump" Solution Bath
8 500 mg/L OH⁻ (0.5M)
11 500 mg/L Na+ (0.5M)

Figure 8. Anion exchange membrane and initial experimental conditions for "leakage" rate experiment.

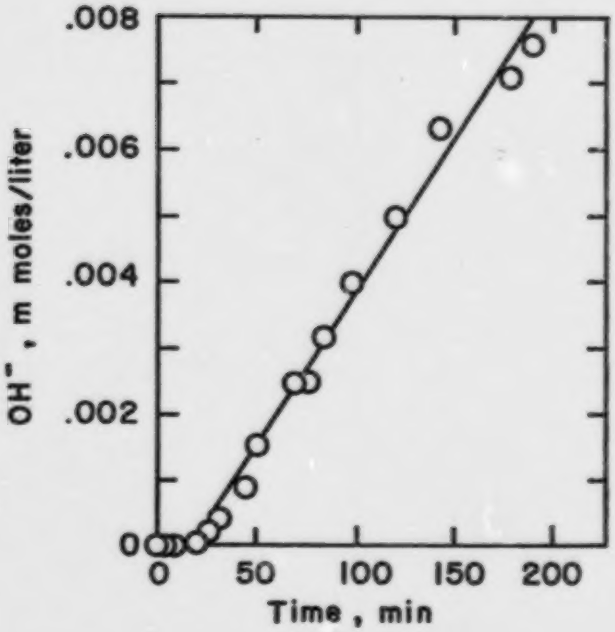

Figure 9. Concentrate bath hydroxide ion accumulation curve using Ionac MA 3475 anion exchange membrane (53 cm^2).

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exchange other cations). The direction of the current study was also along these lines. Calculations were completed to determine what precipitation problems might be encountered in this project, and Donnan dialysis softening experiments were conducted to confirm the feasibility of utilizing the Donnan softening to complete the current project concentration goals. The removal of overall inorganic burden was not necessary to achieve the contractual concentration goals and, therefore, the anion exchange system was not used in the concentration experiments.

As is discussed later in Section 4.A.8, the concentration experiments comprised three stages of membrane processing 1) reverse osmosis concentration to levels approaching inorganic solubility limits, 2) limited softening of the concentrate by using the Nafion^{R} component and a Na^+ pump solution, and 3) final concentration to 50X with the RO membrane. This sequence mimics the previous and anticipated future field concentrations as much as possible while maintaining discrete, identifiable process elements (i.e., RO, Donnan dialysis). An exact duplication of field techniques was not practical due to the increased complexity of interpretation of results from concurrent operation of both RO and Donnan components. Experiments were conducted with the inorganic matrix specified for the study to confirm the feasibility of this approach.

The test to determine the feasibility of using a three-stage, 50X concentration process was designed to evaluate whether or not adequate reduction of critical inorganic ions could be achieved following the anticipated operating protocol. Calculations were made to determine at what levels the most significant salts would precipitate. Table 8 shows the mixed salt matrix required in this study. Table 9 illustrates the potential of precipitate formation for $CaCO_3$ and $CaSO_4$. The likelihood of $CaCO_3$ precipitation is calculated from the Langelier saturation index (LSI) (13). In calculating the LSI, normal operating pH (5.5) was used, and 100% retention of all salts during concentration was assumed. A negative LSI indicates that there should not be a $CaCO_3$ precipitation problem under anticipated conditions in this study.

The potential for $CaSO_4$ precipitation is based on classical chemical solubility product calculations. Solubility product calculations for the inorganic mixture used in this study indicate that $CaSO_4$ precipitation could be expected to occur slightly above a 14X concentration (see Table 9) if no adjustments were made in the calcium or sulfate ion levels. Further calculations indicate 50X concentrations could be achieved, without removal of sulfate, if the calcium were reduced to 1.2 mg/L prior to concentration from 14X to 50X. Experiments were conducted to confirm the feasibility of accomplishing this.

The Donnan softening loop shown in Figure 2 was used for the feasibility determination experiment. Concentration scale equipment was used so that the data could be used directly to predict performance during concentration runs. Figure 10 represents data from the experimental Donnan dialysis softening test. This data is typical of that generated on several similar experiments and demonstrated that 50X volume concentrations may be achieved without precipitation using Donnan softening only, thus eliminat-

TABLE 8. INITIAL INORGANIC SALT MAKEUP OF THE MATRIX WATER

Cations (ppm/mMolar)	Anions (ppm/mMolar)
Na (19.2/0.83)	HCO_3 (50.8/0.83)
Ca (48.1/1.20)	SO_4 (84.7/0.88)
Pb ($19.2 \times 10^{-3}/9 \times 10^{-5}$)	NO_3 ($5.8 \times 10^{-3}/9 \times 10^{-5}$)
Total dissolved cations	67 ppm
Total dissolved anions	159 ppm
Total dissolved solids	226 ppm

TABLE 9. LANGELIER SATURATION INDEX (LSI), $CaSO_4$ ION PRODUCT, AND PRECIPITATION POTENTIALS FOR CALCIUM SALTS OF SULFATE AND CARBONATE

Volume concentration factor (assumes 100% rejection of salts)	LSI	Ion product*** $[Ca][SO_4]$	Precipitation potential $CaCO_3$	Precipitation potential $CaSO_4$
1*	-0.2	1.06×10^{-6}	(-)	(-)
1**	-3.6	1.06×10^{-6}	(-)	(-)
5**	-2.8	2.64×10^{-5}	(-)	(-)
10**	-2.4	1.06×10^{-4}	(-)	(-)
14**	-2.3	2.06×10^{-4}	(-)	(-)
20**	-2.0	4.22×10^{-4}	(-)	(+)

*No pH adjustment

**pH adjustment to 5.5 maximum

***($2.4 \times 10^{-4} = K_{sp}$ of calcium sulfate)

(+) - yes

(-) - no

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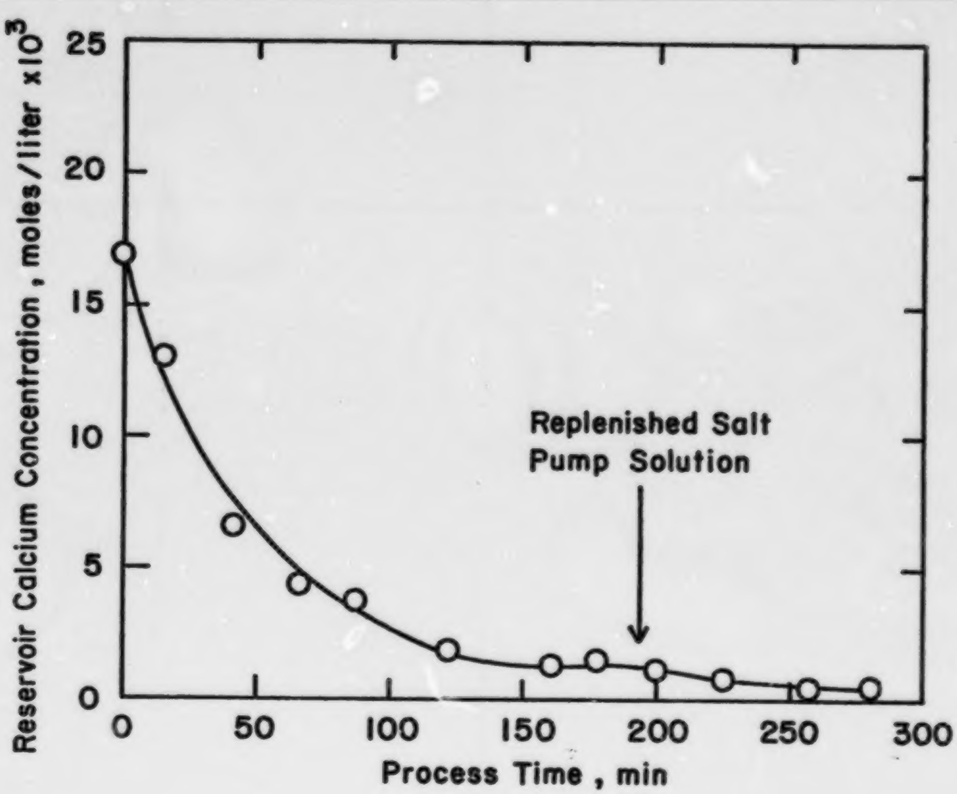

Figure 10. Donnan softening experimental results using the Nafion membranes on 38.5 liters of 14X inorganic matrix water.

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ing the need for the anion exchange system. The exponential response indicates a design limitation rather than Donnan pumping performance. For example, a more linear response can be achieved by increasing the size of the pump bath.

Experimentally, a 38.5 liter (10.2 gallon) volume of 14X inorganic matrix water, as prepared in Appendix C, was recirculated on one side of the membrane. Calcium concentrations were routinely monitored in the recirculating water bath, which was designed to represent the partially concentrated organic spiked water. Calcium concentrations were reduced from better than 17 mM to about 1.5 mM before the chemical pump solution was replenished. The calcium levels were further reduced to 0.5 mM after replenishment of the pump solution. Some NaCl leakage was indicated from the increase in bath chloride levels. NaCl leakage may be minimized by proper manipulation of pump solutions. These tests indicate the feasibility of accomplishing project goals of 50X concentration without precipitation of inorganic salts.

Procedures in the secondary screening evaluations and concentration tests were based on the three-step, 50X concentration protocol. Donnan membrane tests were evaluated using a typical 4 hour maximum processing time which should, according to data in Figure 10, be adequate to prevent the formation of inorganic precipitates.

b. Reverse Osmosis Membranes--

There were no preliminary screening tests performed on the RO membranes. Since there were only two acceptable membrane candidates, it was decided to move directly to test with the commercially available membrane modules and to conduct the screening test with the concentration scale equipment. Laboratory study of the RO membranes was initiated with the secondary screening studies as described in Section 4.A.7.

6. Equipment and Procedures Optimization

The basic equipment used in the secondary membrane screening test and for the concentration experiments has already been described (see Section 4.A.3). Two initial test runs were performed using tap water as a coolant (Run Nos. 589-85 and 589-81). However, temperature control of the concentrate could not be maintained lower than 26°C. For all later experiments, ice water was used as a coolant, and temperature was maintained at 20°C. Three other improvements were made in the test apparatus design to improve overall recoveries. These equipment and procedural modifications are listed below. All the changes were primarily for reduction of solute losses due to volatility.

1. A loose-fitting cover was fabricated for the top of the 55-gallon process drum. The top was designed to minimize air flow currents which, if not controlled, can increase solute losses by sweeping the concentrate surface. The covers sould also help control headspace loss.
2. The fluid return lines for both the reverse osmosis (reject,

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permeate, and bypass) and Donnan softening circulation loop were extended to a point below the minimum expected fluid level in the process drum. This prevented the spraying of return concentrate solutions and minimized volatile solute losses.

3. A double layer of floating spheres (20 mm diameter polypropylene) was applied to the surface of the concentrate. Theory predicts that a single-layer floating sphere blanket can reduce evaporative losses by 87 percent. Actual industrial use has experienced evaporative loss reductions of up to 75 percent. The floating sphere blanket also helps maintain temperature control. Polypropylene balls were selected on the basis of their excellent chemical resistance and inertness.

4. An option for circulating ice water through the cooling coil was added to the system. During the third quarter (when tap water temperatures were below 25°C), process water temperature control at 26 ± 2°C was feasible. During the fourth quarter, ambient water temperatures rose to approximately 30°C and process water control could be held only to 32 ± 2°C. This temperature was adequate for flushing and system blank determination, but was too high to obtain representative data, especially for some of the more volatile solutes (e.g., chloroform).

Tap water cooling was used during flushing and blank determinations, and the control temperature varied with the ambient water temperature. The warmer temperatures experienced with tap water control assisted in flushing and should represent a worst-case situation in the blank determinations. Ambient temperatures in August and September are normally the highest in the New Orleans area, and the 32°C control should therefore represent a maximum.

7. Secondary Membrane Screening

Four membranes were evaluated in the secondary screening tests. The four most promising, as determined in the preliminary evaluations, were the FT-30 and cellulose acetate RO membranes, the Nafion$_R$ cation exchange membrane, and the Ionac MA 3475 anion exchange membrane. Several initial objectives were considered in design of the secondary membrane screening test. Included among these objectives were:

1. To determine what trace organic compounds might leach from the membranes and to determine what effect a free chlorine residual might have on the type of substance(s) leached from the membranes.

2. To determine whether flushing regimes typical of those used in previous RO concentrations were adequate to eliminate contamination from leachable compounds.

3. To provide data sufficient to estimate solute losses to the membranes and other system components.

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4. To determine specific membrane rejections with selected model organic solutes.
5. To determine whether levels of humic acid typical of those experienced in drinking water significantly affected the organic rejections.

A three-stage screening protocol (see Appendices A and B) was developed to evaluate the selected RO and Donnan membranes during the secondary screening. The protocol was designed to be responsive to the stated objectives. The three stages were flushing, system blank determination, and membrane solute screening. The stages used and sampling regimes assigned for each test run were determined by its objectives.

The five subsections below describe objectives, test procedures, and list results of a series of secondary screening experiments. Standard operating procedures (SOPs), as well as any notable exceptions to the SOPs, are referenced. Individual test runs are indicated with a specific run number to aid in discussing a specific test designed with multiple objectives. These same tests are discussed in several locations in the text. All of the results are discussed in Section 4.A.9, which is also structured according to study objectives. Significant conclusions based on the results have already been presented in Section 2.

In the first subsection, on organic free water and solute solubility studies, work done prior to the membrane evaluations is described. The preparation and characterization of the organic free water used for flushing, leaching, and sample preparation are described in this section. Initial solute solubility determinations are also described.

Leaching and chlorine exposure studies (sections 4.A.7.b and 4.A.7.c) were performed primarily to generate data necessary to determine the leachable organics and the effects of chlorine on the leachables from the membrane system.

Data indicating the extent of solute losses (primarily due to adsorption) were obtained in the test described under the subheadings organic solute retention (4.A.7.d) and humic acid exposure (4.A.7.e). These data were determined by the analysis of solute concentrations before and after fixed periods of total solution recirculation. The same tests provided much of the data on instantaneous membrane rejection by analysis of solute levels in the feed and permeate streams after a short equilibration period. Humic acid exposure effects were evaluated by comparing the results of membrane screening tests with and without humic acid present. Additional data for comparing the effects of humic acid were obtained from the concentration test runs (Section 4.A.8).

Since all the test runs were performed using the basic membrane screening procedures (Appendices A and B), data on the adequacy of the flush procedure was obtained from nearly all runs. These data are presented in the discussions on leaching (4.A.7.b), chlorine exposure (4.A.7.c), organic solute retention (4.A.7.d), and humic acid exposure (4.A.7.e).

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a. Organic Free Water and Solute Solubility--

Prior to initiating membrane evaluations, the quality of OFW being produced for use in flushing membrane systems, preparing spike solutions, and post-experiment cleanup was evaluated. The system for producing the OFW was described in Section 4.A.3. OFW quality was examined using several analytical methods.

The OFW was first analyzed for compounds identifiable by GC/FID, then by GC/MS (EPA Method 625), and fnally by GC/ECD. None of the model solutes usually detected by GC/FID (see Appendix G) were detected in the OFW. Acid and base neutral extracts of the OFW which were analyzed by GC/MS (EPA Method 625 for semivolatile priority pollutants) revealed no organic contaminants. Reconstructed chromatograms of the GC/MS analysis are shown in Figure 11. Only internal reference standards were revealed in the analysis. Analysis of the OFW by GC/ECD, which is highly sensitive to halogenated organic compounds, revealed no contaminants. Figure 12 illustrates typical GC/ECD chromatograms of the untreated tap water and of the OFW. Analysis of the OFW for dissolved inorganic salts indicated total dissolved solids at approximately 7 mg/L. Desalting of the tap water feed was accomplished primarily by the reverse osmosis membrane component of the OFW system.

Limited solute solubility experiments were performed prior to initiation of membrane screening and preparation of spike solutions. At the time this test was conducted, only Group 1 model compounds (see Appendix G) were available for use. Target levels of model solutes were 50 times (50X) the required base levels (1X). Additionally, model solute solubilities were checked at 1X and 5X inorganic salt matrix levels and 0.5 and 2.5 percent acetone levels. These variations in the matrices were evaluated to determine if inorganic "salting out" or acetone enhanced solubility effects would be observed. Table 10 shows the results of this limited work.

Nine compounds were included in the solubility screening test. Stearic acid and methylisobutyl ketone analysis had not been validated by the Group 1 methodology and the two chlorinated biphenyls were not in house at the time of the test.

With the exception of bis(2-ethylhexyl)phthalate, the solubility data indicated no significant salting out effects. Unexplained inconsistencies exist in the phthalate data set. Later data from other screening experiments suggests that concentrations approaching 2 mg/L (as observed in the OFW + 0.5% acetone sample, Table 10) are attainable.

No appreciable benefits were realized using the additional acetone. The lower level of acetone was used throughout the screening studies to minimize interactions between acetone and the study membranes. The data (Table 10) suggests that a solubility problem with anthraquinone and 1-chlorododecane may exist.

Membrane screening tests were initiated after a review of the solubility data indicated that adequate levels of most model solutes were attainable under anticipated conditions of the screening test.

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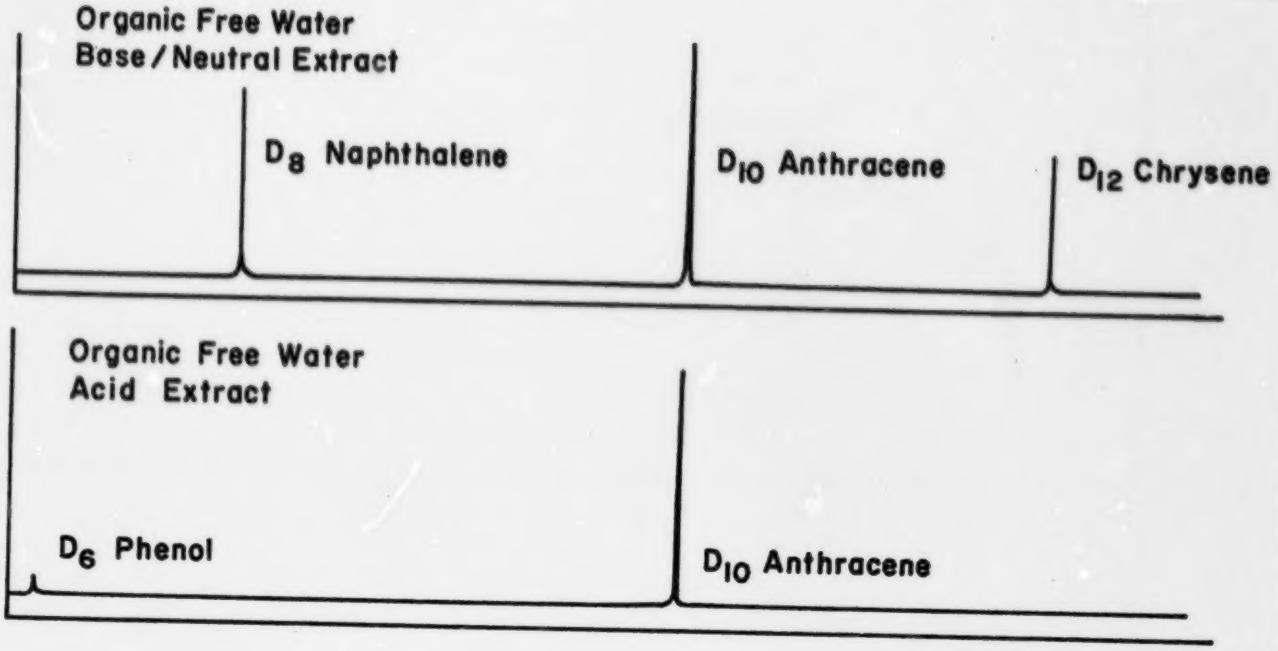

Figure 11. GC/MS chromatograms (EPA Method 625) of organic free water.

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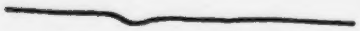
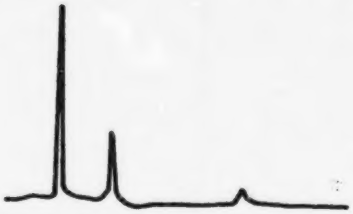


(a) Organic Free Water



(b) Untreated Tap Water

Figure 12. GC/ECD chromatograms of organic free water (a) and untreated tap water (b).

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TABLE 10. SOLUBILITY SCREENING DATA - GROUP 1 COMPOUNDS (ppm)

Model solutes	Stock acetone solution	OFW + 0.5% acetone	OFW + 2.5% acetone	OFW + 1X salt + 0.5% acetone	OFW + 5X salt + 0.5% acetone
isophorone	439(498)*	1.8(2.5)	1.7(2.5)	2.3(2.5)	2.5(2.5)
2,4-dichlorophenol	422(527)	2.5(2.6)	2.3(2.6)	3.1(2.6)	3.0(2.6)
quinoline	449(537)	2.3(2.7)	2.0(2.7)	2.8(2.7)	2.7(2.7)
1-chlorododecane	76(52)	0.14(0.26)	0.16(0.26)	0.10(0.26)	0.10(0.26)
2,6-tert-butyl-4-methylphenol	LA**(500)	3.4(2.5)	2.1(2.5)	2.2(2.5)	1.6(2.5)
caffeine	626(503)	1.7(2.5)	1.8(2.5)	2.0(2.5)	1.8(2.5)
anthraquinone	559(507)	0.2(2.5)	0.3(2.5)	0.4(2.5)	0.3(2.5)
bis(2-ethylhexyl)phthalate	415(500)	2.0(2.5)	0.3(2.5)	0.17(2.5)	0.15(2.5)
biphenyl	480(518)	1.6(2.6)	1.4(2.6)	1.7(2.6)	1.9(2.6)

*Values in parentheses are calculated levels of model solutes expected

**Lab accident

b. Leaching--

One aspect of interest in any system designed to concentrate trace organic chemicals from water is possible leaching of organic compounds from components of the system. Nearly all elements of the RO system under evaluation are fabricated from glass, Teflon, or stainless steel. Very few organics are expected to leach from these materials. However, other components of the concentration system, such as membranes, adhesives, and seals, are made from synthetic organic materials. The existence of these organic based materials necessitated the examination of their contribution, if any, to the aqueous concentrate.

Information on leachable organic materials from membrane system components was derived from the experimental data for several test runs. Some data on leachable organics was obtained as a routine part of the screening tests for organic solute retention which are discussed later in Section 4.A.7.d. Only substances designated as model solutes in this study were assayed for in these tests.

The most extensive examination of membrane systems for organic leachables was in the screening runs designed exclusively for that purpose. Analysis in this series of tests included examination for low molecular weight halogenated compounds (trihalomethanes, THMs), semivolatile priority pollutants by GC/MS (EPA Method 625), as well as the specific model solutes designated for this study. Both series of tests are discussed below, and results are presented.

Leaching results from the series of membrane screening tests designed primarily to study solute retention (Section 4.A.7.d) are presented in Tables 11 through 14. (Nomenclature used in the column headings and test procedures are detailed in Appendix A for RO membranes and Appendix B for Donnan membranes.) Test data from the screening runs are presented by membrane type and include chemical analysis of samples at the beginning of the "system blank" determination ($F_{.08\ \mathrm{hrs}}$)and analysis after a fixed period of total recirculation ($F_{4.0\ \mathrm{hrs}}$). GC/FID chromatograms from two such samples are illustrated in Figures 13 and 14.

Tables 11-14 also list data from the series of experimental runs that was designed specifically to evaluate organic leaching and from the test series to determine effects of chlorine on the leaching process (run numbers 618-16, 618-18, 618-21 and 618-23). The values listed for the leaching test, without chlorine present, were obtained from analysis of system blank samples taken during tests performed following the SOPs in Appendices A and B. The basic SOP was altered slightly by reducing the number of samples required. In these tests, only samples collected at the end of a 4 hr recirculation period were analyzed. GC/MS spectral confirmation of model solutes from this series of tests is also indicated in the tables.

Tables 11-14 represent analysis of only the model solutes used in this study. Tables 15-19 list additional organic compounds tentatively identified by GC/MS and GC/ECD in leaching tests. Results from the chlorine exposure experiments described in the next section are also listed in Tables 11-19.

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TABLE 11. ANALYSIS OF MODEL SOLUTES AT THE BEGINNING AND END OF THE SYSTEM BLANK DETERMINATION ON CELLULOSE ACETATE MEMBRANE (ppm)

	Run 589-59		Run 589-85		Run 618-04		Run 618-30		Run 618-23 (Without Cl_2)		Run 618-23 (With Cl_2)	
	F .08 Hr	F 4.0 Hr	F .08 Hr	F 4.0 Hr	F .08 Hr	F 4.0 Hr	F .08 Hr	F 4.0 Hr	GC/MS Conf.	F 4.0 Hr	GC/MS Conf.	F 4.0 Hr
methylisobutyl ketone	*	*	*	*	*	*	*	*	--	*	--	**
isophorone	ND	ND	ND	ND	ND	ND	ND	ND	--	ND	--	ND
2,4-dichlorophenol	*	*	ND	ND	ND	ND	ND	ND	(5)	0.013	--	ND
quinoline	*	*	ND	ND	ND	ND	ND	ND	--	ND	--	ND
1-chlorododecane	ND	ND	ND	ND	ND	0.006	ND	ND	--	ND	(1)	0.008
biphenyl	ND	ND	ND	ND	ND	ND	ND	ND	(2)	0.005	(2)	0.006
2,6-di-tert-butyl-4-methylphenol	ND	ND	ND	ND	ND	ND	ND	ND	(3)	0.10	--	ND
caffeine	*	*	ND	ND	ND	ND	ND	ND	--	ND	--	ND
stearic acid	*	*	0.30	0.11	0.14	0.03	ND	ND	--	ND	--	ND
anthraquinone	ND	ND	ND	ND	ND	0.009	ND	ND	--	ND	(3)	0.008
2,4'-dichlorobiphenyl	ND	ND	ND	ND	ND	ND	ND	ND	--	ND	--	ND
2,2',5,5'-tetrachlorobiphenyl	ND	ND	ND	ND	ND	0.009	ND	ND	--	ND	--	ND
bis(2-ethylhexyl) phthalate	*	*	LA	ND	ND	ND	ND	ND	--	ND	--	ND
trimesic acid	*	*	*	*	ND	ND	ND	ND	--	#	--	#
furfural	*	*	*	*	ND	ND	ND	ND	--	ND	--	ND·
5-chlorouracil	*	*	*	*	ND	ND	ND	ND	--	ND	--	ND
glycine	*	*	*	*	ND	ND	#	#	--	ND	--	ND
glucose	*	*	*	*	†	†	†	†	--	†	--	†
chloroform	**	**	ND	ND	ND	ND	ND	ND	(4)	ND	(4)	0.003
humic acid	*	*	*	*	*	*	**	**	(4)	**	(4)	**

(1) Not confirmed by GC/MS. Coeluting peak consisting of di-t-butylbenzoquinone and dimethylethylmethoxyphenol was detected at the retention time expected for 1-chlorododecane
(2) Confirmed by GC/MS
(3) Confirmed by extracted ion current profiles techniques (ICP)
(4) Not applicable to GC/MS semivolatile method
(5) GC/MS limit of detection higher than GC/FID

* - Analytical methodology not developed at time of the test
† - Radioisotope method - not assayed in these tests
# - Analytical problems with HPLC columns
** - Not analyzed
LA - Laboratory accident
ND - Not detected
F - Recirculating feed stream
Hr - Hours

TABLE 12. ANALYSIS OF MODEL SOLUTES AT THE BEGINNING AND END OF THE SYSTEM BLANK DETERMINATION ON FILM TEC FT-30 MEMBRANE (ppm)

	Run 589-81		Run 618-09		Run 618-34		Run 618-21 (Without Cl_2)		Run 618-21 (With Cl_2)	
	F .08 Hr	F 4.0 Hr	F .08 Hr	F 4.0 Hr	F .08 Hr	F 4.0 Hr	GC/MS Conf.	F 4.0 Hr	GC/MS Conf.	F 4.0 Hr
methylisobutyl ketone	*	*	*	*	*	*	--	*	--	*
isophorone	ND	ND	ND	ND	ND	ND	--	ND	--	ND
2,4-dichlorophenol	ND	ND	ND	ND	ND	ND	(2)	0.030	--	ND
quinoline	ND	ND	ND	ND	0.013	0.007	--	ND	(3)	0.002
1-chlorododecane	ND	ND	ND	ND	ND	ND	(1)	0.006	(1)	0.006
biphenyl	ND	ND	ND	0.01	ND	ND	--	ND	(2)	<0.005
2,6-di-tert-butyl-4-methylphenol	ND	ND	ND	0.02	ND	ND	--	ND	--	ND
caffeine	ND	ND	ND	ND	ND	ND	--	ND	--	ND
stearic acid	0.46	0.04	0.19	0.39	ND	ND	(5)	0.18	(5)	0.21
anthraquinone	ND	ND	ND	ND	ND	ND	--	ND	--	ND
2,4'-dichlorobiphenyl	ND	ND	ND	ND	ND	ND	--	ND	--	ND
2,2',5,5'-tetrachlorobiphenyl	ND	ND	ND	ND	ND	ND	--	ND	--	ND
bis(2-ethylhexyl) phthalate	ND	0.06	ND	0.05	ND	ND	--	ND	--	ND
trimesic acid	*	*	ND	ND	ND	ND	--	ND	--	ND
furfural	*	*	ND	ND	ND	ND	--	ND	--	ND
5-chlorouracil	*	*	ND	ND	ND	ND	--	ND	--	ND
glycine	*	*	ND	ND	#	#	--	ND	--	ND
glucose	*	*	†	†	†	†	--	†	--	†
chloroform	ND	ND	ND	ND	ND	ND	(4)	0.007	(4)	0.003
humic acid	*	*	*	*	**	**	(4)	*	(4)	*

(1) Not confirmed by GC/MS. Coeluting peak consisting of di-t-butylbenzoquinone and dimethylethylmethoxyphenol was detected at the retention time expected for 1-chlorododecane
(2) confirmed by GC/MS
(3) confirmed by extracted ion current profiles techniques (ICP)
(4) not applicable to GC/MS semivolatile method
(5) GC/MS limit of detection higher than GC/FID

* - Analytical methodology not developed at time of the test
† - Radioisotope method - not assayed in these tests
# - Analytical problems with HPLC columns
** - Not analyzed
ND - Not detected
F - Recirculating feed stream
Hr - Hours

TABLE 13. ANALYSIS OF MODEL SOLUTES AT THE BEGINNING AND END OF THE SYSTEM BLANK DETERMINATION ON NAFION^R MEMBRANES (ppm)

	Run 618-10		Run 618-48		Run 618-18 (Without Cl_2)		Run 618-18 (With Cl_2)	
	F .08 Hr	F 4.0 Hr	F .08 Hr	F 4.0 Hr	GC/MS Conf.	F 4.0 Hr	GC/MS Conf.	F 4.0 Hr
methylisobutyl ketone	*	*	ND	ND	--	*	--	*
isophorone	ND	0.08	ND	ND	(2)	0.03	(2)	0.03
2,4-dichlorophenol	ND	ND	ND	ND	--	ND	--	ND
quinoline	ND	ND	ND	ND	--	ND	(3)	0.002
1-chlorododecane	ND	ND	ND	ND	--	ND	--	ND
biphenyl	ND	ND	ND	ND	--	ND	(2)	0.008
2,6-di-tert-butyl-4-methylphenol	ND	ND	.009	.008	--	ND	--	ND
caffeine	ND	ND	ND	ND	--	ND	--	ND
stearic acid	0.13	0.27	ND	ND	--	ND	(5)	0.36
anthraquinone	ND	ND	0.007	ND	--	ND	(2)	0.100
2,4'-dichlorobiphenyl	ND	ND	ND	ND	--	ND	--	ND
2,2',5,5'-tetrachlorobiphenyl	ND	ND	0.010	0.009	--	ND	(2)	<0.005
bis(2-ethylhexyl) phthalate	ND	ND	ND	ND	(2)	<0.021	(2)	<0.025
trimesic acid	ND	ND	#	#	--	#	--	#
furfural	ND	ND	ND	ND	--	ND	--	ND
5-chlorouracil	ND	ND	ND	ND	--	ND	--	ND
glycine	ND	ND	#	#	--	#	--	#
glucose	†	†	†	†	†	†	--	†
chloroform	ND	ND	ND	ND		0.003	(4)	ND
humic acid	*	*	*	*	*	*	(4)	*

(1) Not confirmed by GC/MS. Coeluting peak consisting of di-t-butylbenzoquinone and dimethylethylmethoxyphenol was detected at the retention time expected for 1-chlorododecane
(2) Confirmed by GC/MS
(3) Confirmed by extracted ion current profiles techniques (ICP)
(4) Not applicable to GC/MS semivolatile method
(5) GC/MS limit of detection higher than GC/FID

* - Analytical methodology not developed at time of the test
† - Radioisotope method-not assayed in these tests
# - Analytical problems with HPLC columns
ND - Not detected

F - Recirculating feed stream
Hr - Hours

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TABLE 14. ANALYSIS OF MODEL SOLUTES AT THE BEGINNING AND END OF THE SYSTEM BLANK DETERMINATION ON IONAC MA 3475 MEMBRANES (ppm)

	Run 618-12		Run 618-16 (Without Cl_2)		Run 618-16 (With Cl_2)	
	F .08 Hr	F 4.0 Hr	GC/MS Conf.	F 3.0 Hr	GC/MS Conf.	F 4.0 Hr
methylisobutyl ketone	*	*	--	*	--	*
isophorone	ND	ND	--	ND	--	ND
2,4-dichlorophenol	ND	ND	(2)	0.02	(2)	0.15
quinoline	0.003	ND	--	ND	--	ND
1-chlorododecane	ND	ND	(1)	<0.005	(1)	0.01
biphenyl	ND	ND	(2)	0.008	(2)	0.02
2,6-di-tert-butyl-4-methylphenol	ND	ND	(2)	0.012	--	ND
caffeine	ND	ND	--	ND	--	ND
stearic acid	0.09	0.06	(5)	0.10	(5)	0.16
anthraquinone	ND	0.03	--	ND	(2)	0.24
2,4'-dichlorobiphenyl	ND	ND	--	ND	--	ND
2,2',5,5'-tetrachlorobiphenyl	ND	ND	(2)	<0.005	(2)	<0.005
bis(2-ethylhexyl) phthalate	ND	ND	(2)	<0.03	(2)	<0.03
trimesic acid	ND	ND	--	#	--	#
furfural	ND	ND	--	ND	--	ND
5-chlorouracil	ND	ND	--	ND	--	ND
glycine	ND	ND	--	ND	--	#
glucose	†	†	--	†	--	†
chloroform	ND	ND	(4)	ND	(4)	0.012
humic acid	*	*	(4)	*	(4)	*

(1) Not confirmed by GC/MS. Coeluting peak consisting of di-t-butylbenzoquinone and dimethylethylmethoxyphenol was detected at the retention time expected for 1-chlorododecane
(2) Confirmed by GC/MS
(3) Confirmed by extracted ion current profiles techniques (ICP)
(4) Not applicable to GC/MS semivolatile method
(5) GC/MS limit of detection higher than GC/FID

* - Analytical methodology not developed at time of the test
† - Radioisotope method - not assayed in these tests
# - Analytical problems with HPLC columns
ND - Not detected
F - Recirculating feed stream
Hr - hours

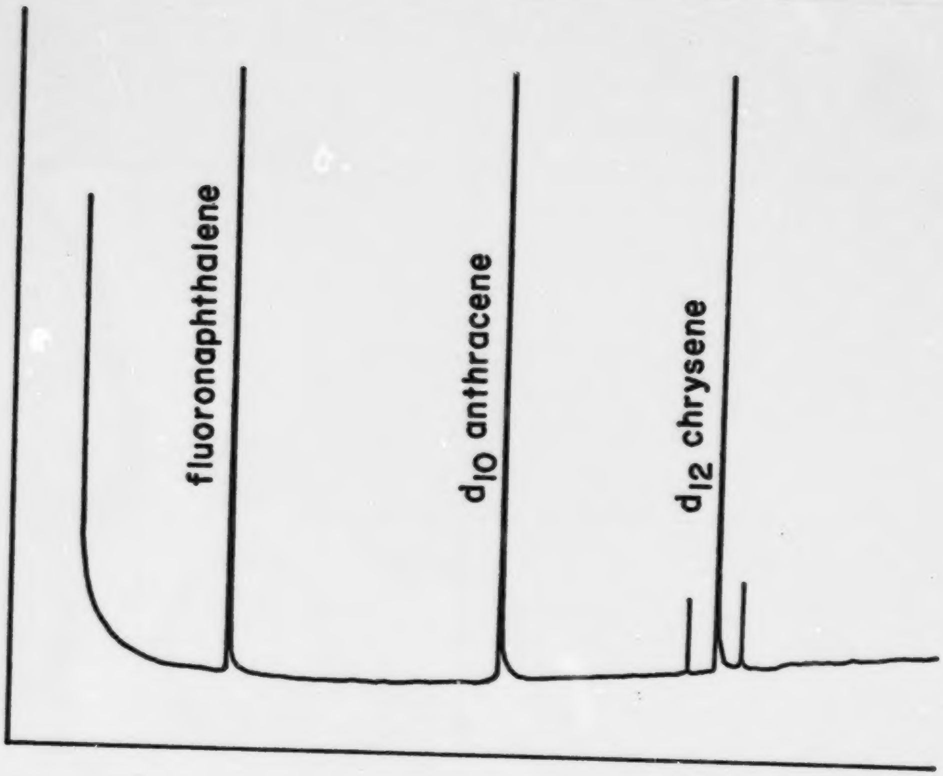

Figure 13. GC/FID analysis of base/neutral extractable compounds from the blank water prior to extended recirculation through the cellulose acetate system ($\mathrm{II}^{F}_{.08}$).

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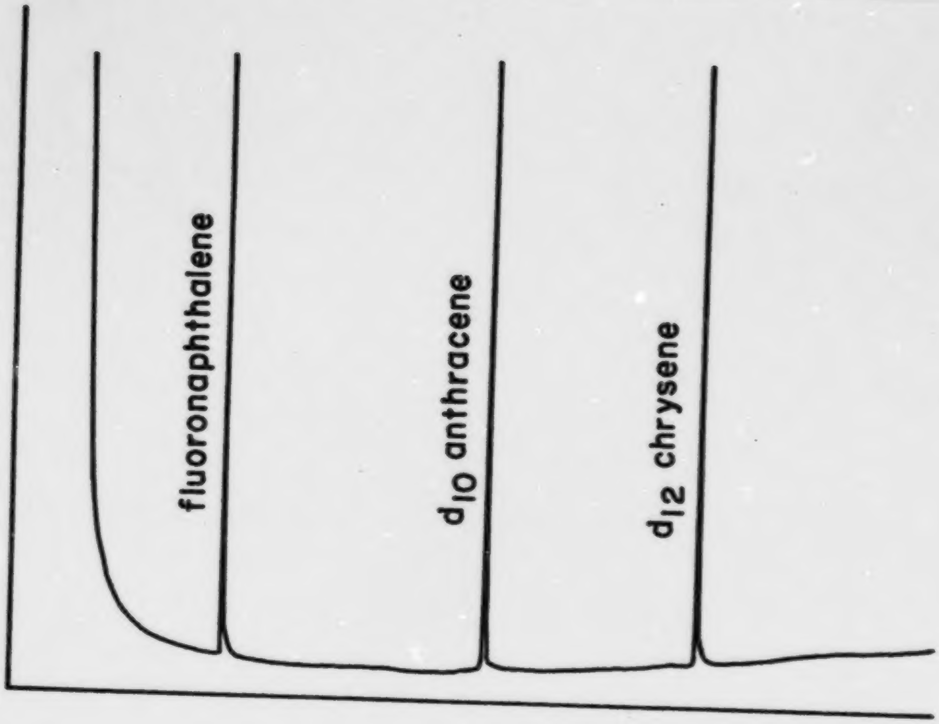

Figure 14. GC/FID analysis of base/neutral extractable compounds after four hours of recirculation through the system $(II^{F}_{4.0})$.

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TABLE 15. ADDITIONAL COMPOUNDS TENTATIVELY IDENTIFIED BY MASS SPECTROMETRY AFTER 4 HOURS OF RECIRCULATION IN THE SYSTEM BLANK AND CHLORINE EXPOSURE TEST ON THE OSMONICS CELLULOSE ACETATE MEMBRANE SYSTEM (TEST RUN 618-23)

System blank before chlorine exposure F 4.0 hr			System blank after chlorine exposure F 4.0 hr		
Isomer formula	Tentative compound identity	RT#	Isomer formula	Tentative compound identity	RT#
$C_{14}H_{20}O_2$	di-t-butylbenzoquinone	15.2	$C_6H_{12}O_2$	cyclohexane-diol	7.6
$C_{11}H_{16}O_2$	dimethylethylmethoxyphenol	(co-elutes at 15.2)	$C_{14}H_{20}O_2$	di-t-butylbenzoquinone	15.2
$C_{19}H_{20}O_4$	butylbenzylphthalate*	27.0	$C_{11}H_{16}O_2$	dimethylethylmethoxyphenol	(co-elutes at 15.2)
			$C_{16}H_{25}O$	di-tert-butylethylphenol*	19.8

#Compound retention time (minutes)
*Compound identification matching through use of previously run in-house standard
F - Recirculating feed stream
hr - hours

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TABLE 16. ADDITIONAL COMPOUNDS TENTATIVELY IDENTIFIED BY MASS SPECTROMETRY AFTER 4 HOUR RECIRCULATION IN THE SYSTEM BLANK AND CHLORINE EXPOSURE TEST ON THE FILM TEC FT-30 MEMBRANE SYSTEM (TEST RUN 618-21)

System blank before chlorine exposure F 4.0 hr			System blank after chlorine exposure F 4.0 hour		
Isomer formula	Tentative compound identity	RT#	Isomer formula	Tentative compound identity	RT#
$C_{14}H_{20}O_2$	di-t-butylbenzoquinone	15.2		unknown	6.9
$C_{11}H_{16}O_2$	dimethylethylmethoxyphenol	(co-elutes at 15.2)	$C_{14}H_{20}O_2$	di-t-butylbenzoquinone	15.2
$C_{16}H_{26}O$	di-t-butylethylphenol*	19.8	$C_{11}H_{16}O_2$	dimethylethylmethoxyphenol	(co-elutes at 15.2)
$C_{14}H_8O_2N_2$	unknown	21.7	$C_{12}H_{20}S$	dibutylthiophene	16.6
			$C_{17}H_{17}O_3N$	no match	17.6
			$C_{14}H_{11}N$	no match	18.5
			$C_{16}H_{25}O$	di-t-butylethylphenol*	19.8
			$C_{14}H_8O_2N_2$	no match	

#Compound retention time (minutes)
*Compound identification matching through use of previously run in-house standard
F - Recirculating feed stream
Hr - hours

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TABLE 17. ADDITIONAL COMPOUNDS TENTATIVELY IDENTIFIED BY MASS SPECTROMETRY AFTER 4 HOUR RECIRCULATION IN THE SYSTEM BLANK AND CHLORINE EXPOSURE TEST ON THE NAFION^R HOLLOW FIBER MEMBRANE SYSTEM (TEST RUN 618-18)

System blank before chlorine exposure F 4.0 hr			System blank after chlorine exposure F 4.0 hr		
Isomer formula	Tentative compound identity	RT#	Isomer formula	Tentative compound identity	RT#
	No peaks above background identified		C_7H_6O	benzaldehyde*	5.7
			$C_6H_{10}Cl_2$	dichlorocyclohexane	7.8
			$C_{14}H_{20}O_2$	di-t-butylbenzoquinone	15.2
			$C_{11}H_{16}O_2$	dimethylethylmethoxyphenol	(co-elutes at 15.2)

#Compound retention time (minutes)
*Compound identification matching through use of previously run in-house standard
F - Recirculating feed stream
Hr - Hours

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TABLE 18. ADDITIONAL COMPOUNDS TENTATIVELY IDENTIFIED BY MASS SPECTROMETRY AFTER 4 HOUR RECIRCULATION IN THE SYSTEM BLANK AND THE CHLORINE EXPOSURE TEST ON THE IONAC MA 3475 MEMBRANE SYSTEM (TEST RUN 618-16)

System blank before chlorine exposure F 4.0 hr			System blank after chlorine exposure F 4.0 hr		
Isomer formula	Tentative compound identity	RT#	Isomer formula	Tentative compound identity	RT#
$C_{14}H_{20}O_2$	di-t-butylbenzoquinone	15.2	C_6H_9Cl	chlorocyclohexene	4.7
$C_{11}H_{16}O_2$	dimethylethylmethoxyphenol	(co-elutes at 15.2)		unknown	6.2
$C_{16}H_{22}O_4$	di-n-butylphthalate	22.3	$C_6H_{10}Cl_2$	dichlorocyclohexane	7.8
				unknown	8.5
				unknown	10.4
				unknown	10.5
				unknown	11.4
			$C_8H_4N_2Cl_2$	dichloronaphthyridine	13.2
			$C_{14}H_{20}O_2$	di-t-butylbenzoquinone	15.2
			$C_{11}H_{16}O_2$	dimethylethylmethoxyphenol	(co-elutes at 15.2)
			$C_{12}H_{14}O_4$	diethylphthalate*	17.2
			C_4	alkylphthalate	21.1
				unknown	22.0
			$C_{16}H_{22}O_4$	di-n-butylphthalate*	22.3
			$C_{19}H_{20}O_4$	butylbenzylphthalate*	27.0

#Compound retention time (minutes) F - Recirculating feed stream Hr - hours
*Compound identification matching through use of previously run in-house standard

TABLE 19. ADDITIONAL VOLATILE CHLORINATED HYDROCARBONS ANALYZED BY GC/ECD AFTER 4 HOUR RECIRCULATION IN THE MEMBRANE SCREENING EXPERIMENTS FOR SYSTEM BLANK AND CHLORINE EXPOSURE EFFECTS

	System blank before chlorine exposure F 4.0 hr			System blank after chlorine exposure F 4.0 hr		
System	$CHCl_2Br$ (ppm)	$CHClBr_2$ (ppm)	$CHBr_3$ (ppm)	$CHCl_2Br$ (ppm)	$CHClBr_2$ (ppm)	$CHBr_3$ (ppm)
Osmonics Cellulose Acetate (Run 618-23)	ND	ND	ND	ND	ND	ND
Film Tec FT 30 (Run 618-21)	ND	0.002	ND	ND	ND	ND
Nafion^R Hollow Fiber (Run 618-18)	0.002	0.002	ND	ND	ND	ND
Ionac MA 3475 (Run 618-16)	ND	ND	ND	0.008	0.005	ND

F - Recirculating feed stream
hr - hours

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c. Chlorine Exposure Studies--

It was desirable to examine the effect that low levels of disinfectant might have on the membranes and other system components since some of these materials might be exposed to active disinfectant during their anticipated use in preparing drinking water concentrates. Free chlorine administered as a sodium hypochorite dilution was selected as a representative challenge. The results of the chlorine exposure tests were monitored by examination of leachable materials from the system when a chlorine solution was recirculated through the membrane system for a fixed period of time. Free chlorine levels were measured at the beginning and end of the recirculation period by the DPD ferrous titrimetric method (14). The free chlorine levels dropped from 2 mg/L to <0.2 mg/L during the 4 hr RO membrane test. In the Donnan membrane test, where recirculation rates are much lower, the chlorine levels dropped from 1.8 mg/L to 0.8 mg/L.

Results of these tests were presented earlier (Tables 11-19). SOPs in Appendices A and B were varied slightly to perform the chlorine exposure experiments. Instead of proceeding directly from the "system blank" phase of the SOP to the "solute screening" phase in the normal sequence, a second system blank was run after dosing the recirculating water with chorine. The effect of the chlorine exposure was determined by examining the recirculating water after the second system blank phase (in the presence of chlorine) was complete.

d. Organic Solute Retention--

This section covers the series of experiments designed to evaluate the ability of the membrane system to separate and retain trace organic substances from water. Two of the initial objectives of this study were to a) determine what portion of the solutes is lost to mechanisms such as volatilization, adsorption, or solubility limitations, and b) determine the membrane's ability to retain trace organic solutes (i.e., its solute rejection).

The focus of these experiments was to evaluate the concentration system/solute behavior without humic acid in the matrix water. Four membranes (cellulose acetate, FT-30, Nafion^{R}, and MA 3475) were tested in this series of membrane/solute screening tests. Two experimental runs, 589-85 and 618-04, were performed with the cellulose acetate membrane in the system. Two test runs, 589-81 and 618-09, were completed on the FT-30 membrane. One test was conducted with each of the ion exchange membranes (Nafion^{R}, 618-10; and MA 3475, 618-12).

The basic three-phase test protocol described at the beginning of Section 4 was used to evaluate the membrane/solute behavior of the four study membranes. The RO membranes (CA and FT-30) were tested by the SOP detailed in Appendix A. The SOP in Appendix B was used as a testing guide for the Donnan membranes. The third phase of both SOPs calls for organically spiking the challenge water immediately after completing the "flush" regime and "system blank" phases of the protocol. The equipment shown previously in Figure 2 was used in these experiments.

The last phase of the test SOP, solute screening, was initiated by

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spiking the OFW with organic solutes according to the SOPs in Appendices A and B. Solute dissolution was monitored in an early test (runs 589-85 and 589-81) by measuring concentrations in the process drum as a functon of mixing time. After examination of these data, a fixed mixing time of 30 minutes was established for the test SOPs. Total recirculation of the organically spiked matrix water through the system was initiated, and the solute screening test begun after the 30 minute mixing period.

Three samples were routinely collected during the solute screening test phase. The recirculating feed water to the RO module was sampled near the beginning (F @ .08 hrs) and at the end (F @ 4.0 hrs) of a 4 hr period of total recirculation (both permeate and reject returned to the process reservoir) to allow calculation of solute losses to the environment and system components. The RO feed samples were collected from the recirculation loop before the RO module. A third sample (P @ 4.0 hrs) taken from the permeate stream, was collected at the same time as the second reservoir sample for the RO membrane evaluations. Membrane solute rejections were calculated from the solute concentrations in the feed/permeate pair of samples collected at the end of the 4 hr period.

For the evaluation of the Donnan membranes, two reservoir samples (F @ .08 hrs and F @ 4.0 hrs) were collected from the recirculating concentrate before the Nafion^R units. These samples provided estimates of organic losses from the system. Since very little water is transported across the Donnan membranes, a permeate sample is not relevant in their testing. Instead, the Donnan membranes were dialyzed aganst a salt solution, and this "strip" or "pump" solution was sampled (S @ 4.0 hrs) at the same time as the last sample from the process reservoir. This allows approximation of the amount of solute lost to the chemical pump solution.

The results of the membrane/solute screening test are presented in Tables 20-25. Tables 20 and 22 include results of spike solution "mixing" evaluations, and all the tables list the levels of solutes in the system blank. The system blank data are the same as those presented earlier in Tables 11-14. Of particular interest here are the data reported in the last three columns. The two recirculating, organically spiked feed samples collected at 5 min (0.08 hr) and 4 hr are listed in the columns headed "F @ .08 hrs" and F @ 4.0 hrs." Results for the permeate stream (RO membranes) or chemical pump solution (Donnan membranes) samples are lited in the last column headed either "P @ 4.0 hrs or S @ 4.0 hrs." Peripheral data collected during the test runs, such as membrane salt rejection, temperature, pH, and pressure, are listed in Table 26. Membrane rejections, solute losses, and other discussions of the data are provided in Section 4.A.9.

e. Humic Acid Exposure Studies--

Humic acid often comprises a major portion of the dissolved organic materials in drinking water. The concentrations of humic acid vary considerably from source to source, but it is not uncommon to find 1-5 mg/L of humid material present in municipal water supplies, especially those from surface sources. For this reason, the effect of humic acid on the membrane systems was surveyed.

TABLE 20. OSMONICS CELLULOSE ACETATE MEMBRANE/ORGANIC SOLUTE SCREENING RESULTS (TEST RUN 589-85 WITHOUT HUMICS) (ppm)

Model solutes	System blank		Spike solution mixing			Membrane solute screening		
	F .08 Hr	F 4.0 Hr	.08 Hr	3.0 Hr	4.0 Hr	F .08 Hr	F 4.0 Hr	P 4.0 Hr
isophorone	ND	ND	2.2		2.2	2.3	2.1	0.67
2,4-dichlorophenol	ND	ND	2.1		2.8	1.8	1.2	3.1
quinoline	ND	ND	2.3		2.3	2.2	1.6	1.0
1-chlorododecane	ND	ND	0.03		0.02	0.02	ND	ND
biphenyl	ND	ND	1.8		1.7	1.2	0.32	0.41
2,6-tert-butyl-4-methylphenol	ND	ND	1.9		2.6	1.2	0.65	0.40
caffeine	ND	ND	2.7		2.5	2.5	0.56	0.51
stearic acid	0.30	0.11	1.3		1.2	0.42	0.27	0.18
anthraquinone	ND	ND	1.4		0.83	0.32	0.17	0.15
bis(2-ethylhexyl)-phthalate	LA	ND	1.8		1.2	0.64	0.11	0.04
chloroform	ND	ND	4.3	3.5	--	1.7	1.3	2.9

ND - Not detected
F - Recirculated feed stream
P - Permeate stream

LA - Lab accident
-- No sample collected

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TABLE 21. OSMONICS CELLULOSE ACETATE MEMBRANE/ORGANIC SOLUTE SCREENING RESULTS (TEST RUN 618-04 WITHOUT HUMICS) (ppm)

Model solutes	System blank F .08 Hr	 F 4.0 Hr	Membrane solute screening F .08 Hr	 F 4.0 Hr	 P 4.0 Hr
isophorone	ND	ND	1.7	2.2	0.56
2,4-dichlorophenol	ND	ND	2.6	1.9	2.0
quinoline	ND	ND	1.8	2.2	2.0
1-chlorododecane	ND	0.006	0.16	0.11	0.03
biphenyl	ND	ND	1.1	0.39	0.42
2,6-tert-butyl-4-methylphenol	ND	ND	0.77	0.90	0.05
caffeine	ND	ND	2.5	2.5	0.55
stearic acid	0.14	0.03	1.1	0.32	ND
2,2,5,5-tetrachlorobiphenyl	ND	0.009	0.10	0.05	ND
anthraquinone	ND	0.009	0.76	0.2	0.18
bis(2-ethylhexyl)phthalate	ND	ND	0.45	ND	ND
trimesil acid	ND	ND	2.1	2.3	0.11
furfural	ND	ND	0.33	1.0	1.9
5-chlorouracil	ND	ND	2.6	2.5	1.5
glycine	ND	ND	1.6	1.9	ND
chloroform	ND	ND	1.2	1.0	1.8

ND - Not detected
F - Recirculating feed stream
P - Permeate stream

TABLE 22. FILM TEC FT-30 MEMBRANE/ORGANIC SOLUTE SCREENING RESULTS (TEST RUN 589-81 WITHOUT HUMICS) (ppm)

Model solutes	System blank F .08 Hr	System blank F 4.0 Hr	Spike solution mixing .08 Hr	Spike solution mixing 1.0 Hr	Spike solution mixing 3.0 Hr	Membrane solute screening F .08 Hr	Membrane solute screening F 4.0 Hr	Membrane solute screening P 4.0 Hr
isophorone	ND	ND	2.1	2.2		2.0	2.0	ND
2,4-dichlorophenol	ND	ND	2.8	2.9		2.1	1.7	0.35
quinoline	ND	ND	2.2	2.3		2.1	1.6	0.20
1-chlorododecane	ND	ND	1.2	1.3		0.45	0.07	ND
biphenyl	ND	ND	1.8	1.6		1.1	0.18	0.02
2,6-tert-butyl-4-methylphenol	ND	ND	3.8	3.4		1.6	0.38	ND
caffeine	ND	ND	2.3	2.2		2.1	2.2	ND
stearic acid	0.46	0.04	1.5	1.7		0.77	0.23	0.08
anthraquinone	ND	ND	0.27	0.43		0.23	0.28	0.03
bis(2-ethylhexyl)-phthalate	ND	0.06	1.5	1.5		0.81	0.13	0.06
chloroform	ND	ND	1.6	--	1.3	0.59	0.37	0.29

ND - Not detected
F - Recirculating feed stream
P - Permeate stream
-- No sample collected

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TABLE 23. FILM TEC FT-30 MEMBRANE/ORGANIC SOLUTE SCREENING RESULTS (TEST RUN 618-09 WITHOUT HUMICS) (ppm)

Model solutes	System blank		Membrane solute screening		
	F .08 Hr	F 4.0 Hr	F .08 Hr	F 4.0 Hr	P 4.0 Hr
isophorone	ND	ND	2.0	1.3	<0.13
2,4-dichlorophenol	ND	ND	2.4	3.1	0.11
quinoline	ND	ND	2.3	1.4	0.06
1-chlorododecane	ND	ND	0.07	0.05	<0.03
biphenyl	ND	ND	1.4	0.05	<0.03
2,6-tert-butyl-4-methylphenol	ND	0.02	1.2	0.32	<0.03
caffeine	ND	ND	2.2	2.2	<0.03
stearic acid	0.19	0.39	0.82	0.21	<0.12
2,2,5,5-tetrachlorobiphenyl	ND	ND	0.08	<0.03	<0.03
anthraquinone	ND	ND	0.33	0.15	<0.03
bis(2-ethylhexyl)phthalate	ND	0.05	0.33	<0.13	<0.13
trimesic acid	ND	ND	2.1	2.1	0.15
furfural	ND	ND	0.15	0.47	0.59
5-chlorouracil	ND	ND	1.6	1.6	ND
glycine	ND	ND	3.4	3.6	ND
chloroform	ND	ND	1.2	1.2	0.19

ND - Not detected
F - Recirculating feed stream
P - Permeate stream

TABLE 24. NAFION^R CATION EXCHANGE MEMBRANE/ORGANIC SOLUTE SCREENING RESULTS (TEST RUN 618-10 WITHOUT HUMICS) (ppm)

Model solutes	System blank F .08 Hr	 F 3.0 Hr	Membrane solute screening F .08 Hr	 F 4.0 Hr	 S 4.0 Hr
isophorone	ND	0.08	2.4	2.7	1.1
2,4-dichlorophenol	ND	ND	3.0	3.1	1.5
quinoline	ND	ND	1.8	1.3	1.5
1-chlorododecane	ND	ND	0.09	0.04	0.07
biphenyl	ND	ND	1.7	1.2	0.62
2,6-tert-butyl-4-methylphenol	ND	ND	1.4	1.4	0.39
caffeine	ND	ND	2.5	--	1.7
stearic acid	0.13	0.27	1.1	1.0	0.19
2,2,5,5-tetrachlorobiphenyl	ND	ND	0.11	0.08	<0.03
anthraquinone	ND	ND	0.34	0.24	0.11
bis(2-ethylhexyl)phthalate	ND	ND	0.50	0.36	0.10
trimesic acid	ND	ND	2.4	2.5	ND
furfural	ND	ND	ND	ND	1.3
5-chlorouracil	ND	ND	2.2	2.1	0.19
glycine	ND	ND	2.5	2.3	0.49
chloroform	ND	ND	2.1	1.2	1.3

ND - Not detected
LA - Lab accident

F - Recirculating feed stream
S - Salt strip (pump) solution

TABLE 25. MA 3475 ANION EXCHANGE MEMBRANE/ORGANIC SOLUTE SCREENING RESULTS (TEST RUN 618-12 WITHOUT HUMICS) (ppm)

Model solutes	System blank F .08 Hr	 F 3.0 Hr	Membrane solute screening F .08 Hr	 F 4.0 Hr	 S 4.0 Hr
isophorone	ND	ND	1.7	1.6	ND
2,4-dichlorophenol	ND	ND	2.6	2.4	ND
quinoline	0.003	ND	1.6	1.6	ND
1-chlorododecane	ND	ND	0.09	0.10	ND
biphenyl	ND	ND	1.40	0.94	ND
2,6-tert-butyl-4-methylphenol	ND	ND	1.5	0.61	ND
caffeine	ND	ND	2.3	2.2	ND
stearic acid	0.09	0.06	1.76	0.40	0.06
2,2,5,5-tetrachlorobiphenyl	ND	ND	0.14	0.04	0.03
anthraquinone	ND	0.03	0.43	0.21	ND
bis(2-ethylhexyl)phthalate	ND	ND	0.54	0.10	ND
trimesic acid	ND	ND	2.1	0.94	**
furfural	ND	ND	2.6	2.2	ND
5-chlorouracil	ND	ND	2.2	2.5	ND
glycine	ND	ND	2.6	2.6	ND
chloroform	ND	ND	1.8	2.1	ND

ND - Not detected
** - Not analyzed

F - Recirculating feed stream
S - Salt strip (pump) solution

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TABLE 26. PERIPHERAL DATA FROM REVERSE OSMOSIS AND DONNAN MEMBRANE SCREENING, CONCENTRATION, AND LEACHING TEST RUNS

Test run	Membrane type	RO membrane salt* rejection (percent)	Operating pressure, psig RO (Donnan)	Initial total dissolved solids† (mg/L)	Temperature (°C)	pH	Osmotic water transported (liters)
589-81 (S)	2	98.5	400	1186	27±4	5-6	--
589-85 (S)	1	94.9	400	1186	27±4	5-6	--
618-04 (S)	1	94.1	400	1186	20±1	5-6	--
618-09 (S)	2	97.3	400	1186	20±1	4.5-5.5	--
618-10 (S)	3	--	(10.5)	1186	19±1	5-7	1.4
618-12 (S)	4	--	(8)	1186	20.5±1	5-7	0.2
618-16 (L)	4	--	(7.5)	1186	21±1	5-7	0.0
618-18 (L)	3	--	(8-11)	1186	21±1	5-7	1.0
618-21 (L)	2	97.1	400	1186	22.5±1	5-6	--
618-23 (L)	1	94.2	400	1186	21±2	5-6	--
618-30 (S)	1	93.2	400	1186	20.8±1	4.5-5.5	--
618-34 (S)	2	95.1	400	1186	20±1	4.5-5.5	--
618-48 (S)	3	--	(11-15)	1186	19±1	5-7	1.0
618-41 (C)	1+3	92.3	400 (13.5)	230	19±2	5-6	1.5
618-51 (C)	2+3	98.6	400 (14)	230	19±2	5-6	1.5
618-57 (C)	2+3	97.9	400 (14)	230	20±2	5-6	1.5
618-65 (C)	2+3	96.7	400	230	20±2	5-6	--

(C)-Concentration run
(S)-Screening run
(L)-Leaching and chlorine exposure test run
1 - Osmonic cellulose acetate membrane
2 - Film Tec^{R} FT-30 membrane
3 - Nafion^{R} hollow fiber membrane
4 - Ionac MA 3475 membrane

*Represents an average of multiple determinations during the test run

†Mixed inorganic salts (29.5% $NaHCO_3$; 50.6% $CaSO_4$; and 19.8% $CaCl_2 \cdot 2H_2O$)

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The data presented in this section was obtained by analysis of samples from test runs performed according to the protocols used in the membrane/solute screening studies (Appendices A and B). The only significant difference between the tests reported here and those reported in the last section was the inclusion of 2 mg/L humic acid in the challenge water matrix. Only the membranes evaluated in the concentration runs (CA, FT-30, and Nafion^{R}) were evaluated for humic acid effects.

The results of the humic acid exposure screening test are listed in Tables 27-29. An evaluation of the observed effects is provided later, in Section 4.A.9. Peripheral data collected during all test runs are provided in Table 26.

8. Membrane Concentration Test

The primary reason this organic recovery scheme was studied was to evaluate its proficiency in obtaining representative concentrated samples of the organic constituents that are present at trace levels in domestic drinking water supplies. The experiments presented thus far have not dealt with actual concentrations but instead have involved screening tests at 50X organic levels. This was done in order to improve the accuracy of analytical results, provide an assessment of the loss of organic material from the concentrate, and to simplify interpretation of the results. In this exercise, a series of concentrations was performed with the study membrane systems, and recovery of specific organic solutes was evaluated. Membrane rejections of specific solutes were again determined.

Figure 3 illustrates the major processing steps in the concentration of 500 liters of organically spiked water. The concentration was designed to reduce 500 liters to 10 liters and incorporates two major types of membrane processes, reverse osmosis concentration and Donnan dialysis softening. First, RO membranes were used to reduce (and concentrate) three 167 liter batches to 13.5 liters each. This was done to allow the 200 liter (55 gallon) scale equipment to be utilized for the concentration of a 500 liter starting volume. RO concentration was temporarily interrupted at 12.6X volumetric concentration. This level of concentration was shown earlier (see Section 4.A.5) to be below inorganic solubility thresholds. At this time, the second membrane process, Donnan softening, was used to adjust the calcium salt levels so that the final concentraton could be obtained.

The RO concentration was continued after the 4 hr Donnan softening treatment was completed. A slight volumetric decrease (with an accompanying increase in concentration factor) was experienced during Donnan softening due to osmotic pumping of water from the concentrate into the salt "pump" solution. The final concentration from 12.7X to 50X concentration factor (CF) was achieved by restarting RO processing. Details of the concentraton procedure are given in Appendix F.

Figure 3 also indicates the samples that were collected at various points during the concentration to monitor its progress. Three streams were sampled during each concentration run: the concentrate (also termed

TABLE 27. OSMONICS CELLULOSE ACETATE MEMBRANE/ORGANIC SOLUTE SCREENING RESULTS (TEST RUN 618-30 WITH HUMICS) (ppm)

Model solutes	System blank F .08 Hr	System blank F 4.0 Hr	Membrane solute screening F .08 Hr	Membrane solute screening F 4.0 Hr	Membrane solute screening P 4.0 Hr
isophorone	ND	ND	1.7	1.8	0.06
2,4-dichlorophenol	ND	ND	1.3	1.0	1.2
quinoline	ND	ND	2.1	2.0	2.0
1-chlorododecane	ND	ND	0.14	0.05	0.02
biphenyl	ND	ND	1.1	0.29	0.44
2,4-dichlorobiphenyl	ND	ND	<0.05	<0.05	ND
2,2',5,5'-tetrachlorobiphenyl	ND	ND	0.10	<0.050	0.01
2,6-di-tert-butyl-4-methylphenol	ND	ND	2.1	0.36	0.10
caffeine	ND	ND	2.2	2.1	0.56
anthraquinone	ND	ND	1.5	0.27	0.23
stearic acid	ND	ND	1.6	<0.25	<0.025
bis(2-ethylhexyl)phthalate	ND	ND	1.7	<0.25	<0.025
trimesic	ND	ND	2.2	2.1	<0.2
furfural	ND	ND	2.2	<0.05	0.26
5-chlorouracil	ND	ND	2.7	2.6	1.4
chloroform	ND	ND	1.3	0.42	1.3

ND - Not detected
F - Recirculating feed stream
P - Permeate stream

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TABLE 28. FILM TEC FT-30 MEMBRANE/ORGANIC SOLUTE SCREENING RESULTS (TEST RUN 618-34 WITH HUMICS) (ppm)

Model solutes	System blank F .08 Hr	 F 4.0 Hr	Membrane Solute Screening F .08 Hr	 F 4.0 Hr	 P 4.0 Hr
isophorone	ND	ND	1.2	1.1	<0.13
2,4-dichlorophenol	ND	ND	1.4	1.2	<0.03
quinoline	0.013	0.007	1.6	1.5	0.04
1-chlorododecane	ND	ND	0.06	<0.05	<0.025
biphenyl	ND	ND	0.92	0.35	<0.025
2,4-dichlorobiphenyl	ND	ND	<0.05	<0.05	<0.025
2,2',5,5'-tetrachlorobiphenyl	ND	ND	0.07	<0.05	<0.025
2,6-di-tert-butyl-4-methylphenol	ND	ND	1.8	0.53	<0.025
caffeine	ND	ND	1.7	1.6	<0.03
anthraquinone	ND	ND	0.83	0.23	<0.025
stearic acid	ND	ND	0.82	<0.25	<0.13
bis(2-ethylhexyl)phthalate	ND	ND	1.0	<0.25	<0.13
trimesic acid	ND	ND	1.7	1.5	<0.05
furfural	ND	ND	ND	ND	ND
5-chlorouracil	ND	ND	2.1	2.0	0.58
chloroform	ND	ND	0.92	0.60	0.07

ND - Not detected
F - Recirculating feed stream
P - Permeate stream

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TABLE 29. NAFION^{R} CATION EXCHANGE MEMBRANE/ORGANIC SOLUTE SCREENING RESULTS (TEST RUN 618-48 WITH HUMICS) (ppm)

Model solutes	System blank F .08 Hr	System blank F 3.0 Hr	Membrane solute screening F .08 Hr	Membrane solute screening F 4.0 Hr	Membrane solute screening S 4.0 Hr
isophorone	ND	ND	1.5	1.2	0.13
2,4-dichlorophenol	ND	ND	1.4	1.6	0.15
quinoline	ND	ND	1.7	0.44	0.36
1-chlorododecane	ND	ND	0.17	0.12	ND
biphenyl	ND	ND	1.2	0.86	0.10
2,2',5,5'-tetrachlorobiphenyl	0.010	0.009	0.25	0.18	0.013
2,6-di-tert-butyl-4-methylphenol	0.009	0.008	0.78	0.73	ND
caffeine	ND	ND	2.4	2.0	0.29
anthraquinone	0.007	ND	2.2	1.6	0.008
stearic acid	ND	ND	2.3	2.2	0.08
bis(2-ethylhexyl)phthalate	ND	ND	1.9	1.8	0.03
furfural	ND	ND	1.9	1.8	1.0
5-chlorouracil	ND	ND	2.0	1.4	*
chloroform	ND	ND	2.3	1.4	0.44
methylisobutyl ketone	ND	ND	2.4	1.9	0.46

ND - Not detected
F - Recirculating feed stream
S - Salt strip (pump) solution
*Not analyzed

"feed" and designated F); the RO permeate, designated P; and the salt pump solution, designated S. Samples are indicated at the extreme left side of Figure 3, along with the target concentration factor. The samples are also indicated on the flow chart by asterisks. The three feed samples collected at CF=1 were composited prior to analysis.

Three membrane concentrations were performed following the testing protocol outlined in Figure 3 and detailed in Appendix F. The cellulose acetate RO membrane was tested first. Donnan dialysis was operated in the softening mode to adjust inorganic salt balances. No humic acid was present in this test. The second concentration was basically a repeat of this test, with the FT-30 membrane substituted for cellulose acetate in the RO system. The third and final concentration run was designed to evaluate the impact of humic acid on the concentration. The final run was a repeat of the FT-30 concentration run except for the presence of humic acid in the test matrix.

Data from the three concentration runs are presented in Tables 30-35. Tables 30 and 31 report data from the cellulose acetate RO membrane concentration (test run 618-41). Table 30 lists the concentration of model solutes in the concentrate (feed-F) as the volumetric concentration factor increases. The first three columns show results from samples in which concentraton changes result from the first stage RO concentration. The third and fourth columns are from the concentrate at the beginning and end of the Donnan softening step. The concentration changes shown in the last three columns are due to the final stage RO concentration. Table 31 lists analysis of RO feed (concentrate) and permeate pairs collected at volumetric concentration factors of 8X and 40X. Tables 32 and 33 provide similar data for the FT-30 concentration test without humic acid present. Tables 34 and 35 list data for the FT-30 membrane concentration performed with humic acid in the test matrix.

The humic acid data shown in Tables 34 and 35 result from a test run (618-65) that was performed separately due to the late development of analytical methodology for humic acid. The other model solutes were not included in the test matrix during test run 618-65.

Peripheral process data such as salt rejection, pressure, solution pH, and temperature for all the concentration test runs, as well as for the membrane screening test, are listed in Table 26.

9. Discussion of Membrane Test Results

In this section, each of the research elements is discussed with respect to the data presented in Sections 4.A.7 and 4.A.8. Significant trends and conclusions are highlighted. For clarity, the sequence of the discussion follows that established in Sections 4.A.7 and 4.A.8. Some redundancy was necessary due to the multifunctional test procedures used. Subject areas which are discussed include leaching of compounds from membranes systems and the effect of chlorine on the types of leachable substances. Membrane rejections determined from the screening and concentration runs are compiled and compared. Components that require con-

TABLE 30. DATA FROM CELLULOSE ACETATE/DONNAN SOFTENING MEMBRANE CONCENTRATION (TEST RUN 618-41). NO HUMIC ACID PRESENT IN WATER MATRIX (ppm) (1) (ppm)

Model solutes	Model solute concentration					
	$F_{CF=1}$	$F_{CF=8}$	$F_{CF=12.6}$	$F_{CF=12.7}$	$F_{CF=40}$	$F_{CF=50}$
isophorone	0.052	0.187	0.290	0.090	0.250	0.220
2,4-dichlorophenol	0.030	0.020	0.020	0.020	0.021	0.022
quinoline	0.006	ND	0.006	0.012	0.006	0.005
1-chlorododecane	0.010	ND	0.025	0.017	0.036	0.025
biphenyl	0.043	0.016	0.015	ND	0.011	0.009
2,4-dichlorobiphenyl	----------Laboratory Accident----------					
2,2',5,5'-tetrachlorobiphenyl	0.005	ND	ND	0.020	ND	ND
2,6-di-tert-butyl-4-methylphenol	0.007	0.008	0.023	0.025	0.013	0.012
caffeine	0.055	0.100	0.290	0.190	0.450	0.610
anthraquinone	0.056	0.038	0.031	ND	0.009	0.019
stearic acid	0.048	ND	0.030	0.026	ND	ND
bis(2-ethylhexyl)phthalate	ND	ND	0.026	0.038	ND	ND
furfural	ND	ND	ND	ND	ND	ND
5-chlorouracil	ND	0.109	ND	ND	0.13	0.16
glycine	ND	ND	ND	ND	ND	ND
trimesic acid	----------Laboratory Accident----------					
glucose	0.040	0.215	0.144	0.146	0.401	0.477
chloroform	0.048	0.021	0.020	0.013	ND	0.010
methylisobutyl ketone	0.044	0.059	0.059	0.054	0.044	0.054

ND - Not detected
F - Feed sample
CF - Concentration factor (volumetric)

(1) Matrix water includes mixed inorganic salts to 226 mg/L total dissolved solids

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TABLE 31. FEED/PERMEATE SAMPLE PAIR ANALYSIS FROM CELLULOSE ACETATE/DONNAN SOFTENING MEMBRANE CONCENTRATION RUN 618-41). NO HUMIC ACID PRESENT IN WATER MATRIX (1) (ppm)

Model solutes	Model solute concentration					
	$F_{CF=8}$	$P_{CF=8}$	Percent Rejection	$F_{CF=40}$	$P_{CF=40}$	Percent Rejection
isophorone	0.187	0.049	74	0.250	0.098	61
2,4-dichlorophenol	0.020	0.024	-20	0.021	0.033	-57
quinoline	ND	0.005	--	0.006	ND	>17†
1-chlorododecane	ND	ND	--	0.036	0.008	78
biphenyl	0.016	0.021	-31	0.011	0.018	-64
2,4-dichlorobiphenyl	----------Laboratory Accident----------					
2,2',5,5'-tetrachlorobiphenyl	ND	ND	--	ND	ND	--
2,6-di-tert-butyl-4-methylphenol	0.008	ND	>38†	0.013	ND	>62†
caffeine	0.100	0.033	67	0.450	0.150	67
anthraquinone	0.038	0.042	-11	0.009	0.043	-378
stearic acid	ND	ND	--	ND	ND	--
bis(2-ethylhexyl)phthalate	ND	ND	--	ND	ND	--
furfural	ND	ND	--	ND	ND	--
5-chlorouracil	0.110	0.075	32	0.127	0.071	44
glycine	ND	ND	--	ND	ND	--
trimesic acid	----------Laboratory Accident----------					
glucose	0.215	0.008	96	0.401	0.015	96
chloroform	0.021	0.027	-29	ND	0.012	<-20†
methylisobutyl ketone	0.059	0.049	17	0.044	0.053	-20

ND - Not detected

F - Feed sample; P - Permeate sample; CF - Concentration factor (volumetric)

† - Greater than (>) values are calculated using the analytical detection limit where compounds were not detected [e.g., %R = (1-P/F) 100 with F = 90 and P< detection limit = 9; therefore, a P<9 gives %R>90]. "Less than" values are determined in a like manner

(1) Matrix water includes mixed inorganic salts to 226 mg/L total disssolved solids

-- Insufficent data to calculate value

TABLE 32. DATA FROM FT-30/DONNAN SOFTENING MEMBRANE CONCENTRATION (TEST RUN 618-51). NO HUMIC ACID PRESENT IN WATER MATRIX (1) (ppm)

Model solutes	Model solute concentration					
	$F_{CF=1}$	$F_{CF=8}$	$F_{CF=12.6}$	$F_{CF=12.7}$	$F_{CF=40}$	$F_{CF=50}$
isophorone	0.050	0.300	0.520	0.500	1.53	1.86
2,4-dichlorophenol	0.040	0.210	0.350	0.340	0.970	1.07
quinoline	0.050	0.270	0.460	0.110	0.660	0.480
1-chlorododecane	0.009	0.040	0.060	0.006	0.140	0.160
biphenyl	0.050	0.110	0.130	0.050	0.160	0.160
2,4-dichlorobiphenyl	----------Laboratory Accident----------					
2,2',5,5'-tetrachlorobiphenyl	ND	0.008	0.005	ND	0.013	0.013
2,6-di-tert-butyl-4-methylphenol	ND	0.030	0.010	0.030	0.110	0.110
caffeine	0.050	0.310	0.550	0.090	1.67	1.39
anthraquinone	0.050	0.210	0.190	0.090	0.060	0.210
stearic acid	ND	ND	ND	ND	ND	ND
bis(2-ethylhexyl)phthalate	ND	0.130	ND	ND	0.200	0.035
furfural	ND	0.128	0.092	ND	0.226	0.170
5-chlorouracil	ND	0.362	0.663	0.574	1.82	2.25
glycine	ND	ND	ND	ND	0.054	ND
trimesic acid	----------Laboratory Accident----------					
glucose	0.036	0.235	0.134	0.131	0.430	0.437
chloroform	0.045	0.200	0.220	0.204	0.490	0.460
lead	0.012	0.057	0.092	0.028	0.083	0.065
methylisobutyl ketone	0.040	0.200	0.400	0.270	1.150	1.220

ND - Not detected F - Feed sample CF - Concentration factor (volumetric)

(1) Matrix water includes mixed inorganic salts to 226 mg/L total disssolved solids

TABLE 33. FEED/PERMEATE SAMPLE PAIR ANALYSIS FROM FT-30/DONNAN SOFTENING MEMBRANE CONCENTRATION (TEST RUN 618-51). NO HUMIC ACID PRESENT IN WATER MATRIX (1) (ppm)

Model solutes	Model solute concentration					
	$F_{CF=8}$	$P_{CF=8}$	Percent rejection	$F_{CF=40}$	$P_{CF=40}$	Percent Rejection
isophorone	0.300	ND	>91†	1.53	0.006	99
2,4-dichlorophenol	0.210	0.020	91	0.970	0.040	96
quinoline	0.270	0.002	99	0.660	0.012	98
1-chlorododecane	0.040	0.007	83	0.140	ND	>96†
biphenyl	0.110	ND	>95†	0.160	ND	>97†
2,4-dichlorobiphenyl	------------------------Laboratory Accident------------------------					
2,2',5,5'-tetrachlorobiphenyl	0.008	ND	>38†	0.013	0.010	23
2,6-di-tert-butyl-4-methylphenol	0.030	ND	>83†	0.110	ND	>95†
caffeine	0.310	0.015	95	1.67	ND	>99†
anthraquinone	0.210	ND	>98†	0.060	0.008	87
stearic acid	ND	ND	--	ND	0.040	--
bis(2-ethylhexyl)phthalate	0.130	ND	>81†	0.200	ND	>88†
furfural	0.128	0.050	61	0.226	0.114	36
5-chlorouracil	0.362	ND	>86†	1.82	ND	>97†
glycine	ND	ND	--	0.054	ND	>7†
trimesic acid	------------------------Laboratory Accident------------------------					
glucose	0.235	0.001	99	0.430	0.002	99
chloroform	0.200	ND	>88†	0.490	0.045	91
lead	0.057	0.020	65	0.083	0.034	59
methylisobutyl ketone	0.200	0.010	95	1.150	0.012	99

ND - Not detected

F - Feed sample, P - Permeate sample, CF - Concentration factor (volumetric)

† - Greater than (>) values are calculated using the analytical detection limit where compounds were not detected [e.g., %R = (1-P/F) 100 with F=90 and P< detection limit = 9; therefore, a P<9 gives %R>90]

(1) Matrix water included mixed inorganic salts to 226 mg/L total disssolved solids

-- Insufficient data to calculate value

TABLE 34. DATA FROM FT-30/DONNAN SOFTENING MEMBRANE CONCENTRATION (TEST RUN 618-57). HUMIC ACID PRESENT IN WATER MATRIX (1) (ppm)

Model solutes	Model solute concentration					
	$F_{CF=1}$	$F_{CF=8}$	$F_{CF=12.6}$	$F_{CF=12.7}$	$F_{CF=40}$	$F_{CF=50}$
isophorone	ND	ND	ND	ND	0.070	ND
2,4-dichlorophenol	0.040	0.340	0.390	0.350	0.870	1.03
quinoline	0.060	0.370	0.140	0.070	0.500	0.360
1-chlorododecane	0.007	0.050	ND	0.006	0.140	0.170
biphenyl	0.030	0.140	ND	ND	ND	0.120
2,4-dichlorobiphenyl	0.030	0.030	ND	0.010	ND	0.010
2,2',5,5'-tetrachlorobiphenyl	ND	ND	0.010	0.007	0.030	ND
2,6-di-tert-butyl-4-methylphenol	0.010	0.010	0.014	0.010	0.006	0.010
caffeine	0.060	0.410	0.050	0.052	1.250	1.600
anthraquinone	0.060	0.120	0.009	ND	0.050	0.150
stearic acid	0.056	ND	0.070	0.060	0.050	0.090
bis(2-ethylhexyl)phthalate	0.050	0.310	0.070	0.080	0.200	0.130
furfural	ND	0.063	ND	ND	ND	ND
5-chlorouracil	0.054	0.096	0.132	0.256	1.00	1.21
glycine	ND	0.086	ND	ND	0.174	ND
trimesic acid	-----------------------Laboratory Accident-----------------------					
glucose	.052	0.231	0.131	0.133	0.330	0.420
chloroform	0.044	0.207	0.180	0.175	0.407	0.460
lead	0.024	0.134	0.060	0.054	0.264	0.220
methylisobutyl ketone	0.042	0.310	0.150	0.060	0.730	0.860
humic acid	1.80	5.97	11.30	12.20	44.60	48.60

ND - Not detected
F - Feed sample
CF - Concentration factor (volumetric)
(1) Matrix water included mixed inorganic salts to 226 mg/L total disssolved solids

TABLE 35. TABULATION OF FEED/PERMEATE SAMPLE PAIR ANALYSIS FROM FT-30/DONNAN SOFTENING MEMBRANES CONCENTRATION (TEST RUN 618-57). HUMIC ACID PRESENT IN WATER MATRIX (1) (ppm)

Model solutes	Model solute concentration					Percent Rejection
	$F_{CF=8}$	$P_{CF=8}$	Percent Rejection	$F_{CF=40}$	$P_{CF=40}$	
isophorone	ND	ND	--	0.070	ND	>64†
2,4-dichlorophenol	0.340	0.008	98	0.870	0.050	94
quinoline	0.370	0.001	99	0.500	ND	>99†
1-chlorododecane	0.050	ND	>90†	0.140	ND	>96†
biphenyl	0.140	ND	>96†	ND	ND	--
2,4-dichlorobiphenyl	0.030	ND	>83†	ND	ND	--
2,2',5,5'-tetrachlorobiphenyl	ND	ND	--	0.030	ND	>83†
2,6-di-tert-butyl-4-methylphenol	0.010	ND	>50†	0.006	ND	>17†
caffeine	0.410	0.010	98	1.250	0.010	99
anthraquinone	0.120	ND	>96†	0.050	ND	>90†
stearic acid	ND	ND	--	0.050	ND	>50†
bis(2-ethylhexyl)phthalate	0.310	ND	>92†	0.200	ND	>88†
furfural	0.063	ND	>21†	ND	ND	--
5-chlorouracil	0.096	ND	>48†	1.001	ND	>95†
glycine	0.086	ND	>42†	0.174	ND	>71†
trimesic acid	----------------------Laboratory Accident----------------------					
glucose	0.231	0.001	99	0.330	0.002	99
chloroform	0.207	ND	>88†	0.407	0.039	90
lead	0.134	0.086	36	0.264	0.021	92
methylisobutyl ketone	0.310	ND	>99†	0.730	0.009	99
humic acid	5.97	ND	>92	44.60	ND	>99

ND - Not detected

F - Feed sample; P - Permeate sample; CF - Concentration factor (volumetric)

† - Greater than (>) values are calculated using the analytical detection limit where compounds were not detected [e.g., %R = (1-P/F) 100 with F = 90 and P< detection limit = 9; therefore, a P<9 gives %R>90].

(1) Matrix water included mixed inorganic salts to 226 mg/L total disssolved solids

-- Insufficient data to calculate value.

sideration in a system mass balance (i.e., solute loss due to membrane permeation, solute adsorption, and Donnan dialysis) are introduced and discussed. Mass balances for the concentration system are presented, and solute levels in various components of the system are estimated. Overall system recoveries are calculated, with corrections made for solute losses due to adsorption. Mass recoveries actually experienced for the model solutes in the concentration system are presented. Suggestions are made for changes in field collection of sample concentrates to improve solute recoveries over those experienced in this study.

a. Organic Free Water--

A multistage water treatment system incorporating activated carbon filtration, 5 micron sediment filtration, reverse osmosis filtration, and 0.2 micron bacterial filtration was used to condition New Orleans tap water for use in the study. Gas chromatographic analysis, using mass spectrometric, flame ionization, and electron capture detection, revealed no obvious residual organic contamination (see Figures 11 and 12, Section 4.A.7). The inorganic quality of the OFW was evaluated by determining calcium levels and estimating the total dissolved solids levels (i.e., via conductivity measurement). Considering the objectives of the study and the anticipated methods of accomplishing these objectives, the quality of the OFW was judged to be acceptable. OFW prepared with the four-stage filtration system was used throughout the study.

b. Model Solute Solubility--

A preliminary evaluation of the solubility of model organic solutes was conducted early in the study to establish the validity of anticipated spiking procedures. Analytical methodologies had not been established for all of the model solutes at the time the solubility evaluation was conducted, but most of the Group 1 compounds with confirmed methodologies (Appendix G) were examined. Group 1 contains the least water soluble among the designated solutes and should represent a stringent solubility challenge.

The anticipated spiking procedure specified the use of acetone as a carrier solvent to facilitate dosing the test water. Therefore, it was desirable to know the effect of acetone concentration on solute solubility. A second unknown was the effect of inorganic salt levels. A solubility experiment was designed to screen the effect of these two variables upon the solubilization of the Group 1 solutes. Solute levels in this screening were targeted at 50 times those required as starting levels for the concentration test. Two levels of acetone carrier solvent (0.5 and 2.5%) and two inorganic salt levels (1X and 5X) were selected to represent reasonable extremes. The results of the solubility screening were presented in Table 10, Section 4.A.7.

The data showed no conclusive "salting out" effects at the higher salt levels and no appreciable benefit in using the higher concentration of acetone carrier solvent. Bis (2-ethylhexyl)phthalate exhibited some erratic behavior which was concluded to be not significant in view of later results. There was some evidence of solubility complications with anthraquinone and to some extent with 1-chlorododecane. However, in light of the analytical difficulties encountered in this program, the occasional data scatter, and the limited nature of this cursory examination, the solubility problems indicated cannot be considered conclusive without further examination. Since the general results of the solubility screening were favorable, studies of the membrane systems were initiated.

c. System Blank Studies--

Important considerations in any concentration process are the type, level, and number of trace contaminants which may be imparted to the sample from the system itself. Leaching of organic compounds from the membranes and system components was studied in two series of tests designed at two levels of scrutiny. Results were presented in Tables 11-19 of Section 4.A.7.

In the first level of evaluation, samples were examined only for the model solutes defined in this study. The results of analysis of beginning and ending "system blank" samples for each membrane studied were listed in Tables 11-14. Examination of the beginning and ending samples (F @ .08 and F @ 4.0) shows sporadic occurrences of several of the Group 1 model solutes. Except for stearic acid, nearly all the measurable values occur at less than 2-3 times the absolute detection limits. At this level, analytical errors increase, and matrix interferences become more critical.

Stearic acid was observed routiely in all samples and blanks in the early portions of the study. Several unsuccessful efforts were made to find the source of this apparent contamination. It was never determined whether these numbers were real, but the problem was resolved with the adoption of an alternate surrogate standard for stearic acid in the standard analytical procedure (Appendix G). Although stearic acid values are reported from the early test, they are viewed skeptically due to their unexplained occurrence and disappearance.

Two general observations reinforce the overall low significance assigned to the occurrences of taces of organics 1) the occurrences are not consistently encountered, at least where adequate data exists to make this assessment and 2) many times the quantity of trace organic leachate decreases or is absent altogether in the sample taken after four hours recirculation. It appears, from results of the routine screenings for leachable compounds, that the existence of model solutes in the system blanks is sporadic, at trace levels and probably represents slow, reversible adsorption and desorption of spike organic solutes from earlier exposures to the membrane.

Potential leaching of organic compounds from the membrane systems was examined in more detail in a second series of tests where GC/MS analysis was used in addition to the routine GC/FID, GC/ECD, and HPLC methodologies. This allowed for the examination and identification of organic compounds other than model solutes normally studied in the project. In this series of tests, the effect of chlorine exposure on the types of leachable organics recovered in the blanks was also examined. Data for the model solute analysis listed in Tables 11-14 showed the same general trends that were observed in the routine screening test. Low levels of model solutes occurred sporadically for all the membrane types with no strong trends or consistency of results evident.

The membrane system was charged with 2 mg/L free chlorine after the first 4 hr blank (determination of leachable compounds with no chlorine present) sample was collected. A second blank sample was secured after an additional 4 hr of recirculation to examine the effects of chlorine exposure. Results from the analysis of this sample are listed in the last column of Tables 11-19. As mentioned, the analysis for model solutes (Tables 11-14) did not reveal any significant variations from earlier tests, but a greater number and variety of compounds were detected by GC/MS (Tables 15-19) in tests with chlorine present.

Three compounds were consistently identified in the leachate studies: di-t-butylbenzoquinone, dimethylethylmethoxyphenol, and di-tert-butylethylphenol. Such a pattern in the four leachate runs was not anticipated since there are distinct differences between the materials exposed. In addition, the OFW was produced while exposed to the same type of materials as in the RO membrane trials. These compounds were used in the GSRI laboratory approximately a year earlier in studies of the effluents of energy facilities. It appears, therefore, that these compounds may be laboratory contaminants rather than system leachates.

The cellulose acetate and Nafion^{R} membranes exhibited the lowest increase in number of leached organics after exposure to chlorine. In the test of the cellulose acetate membrane, cyclohexane-diol was detected after chlorine exposure. The coeluting peak was still present, but the butylbenzylphthalate was no longer detectable. None of the compounds detected in the cellulose acetate blank after chlorine exposure were chlorinated substances. The coeluting peak detected in all samples was again present in the Nafion^{R} membrane system blank after chlorine exposure. Two additional compounds, benzaldehyde and dichlorocyclohexane, were detected. This was the first appearance of a likely chlorination by-product.

Analysis of the FT-30 system blank after chlorine exposure revealed the presence of several moe organic substances than were detected in the system blank for the cellulose acetate RO membrane system. The coeluting peak at 15.2 minutes was present again in this sample and probably did not originate from the FT-30 membrane or the chlorine exposure since it was present both prior to chlorine exposure and all the other membrane system blanks having detectable levels of leachates. The di-t-butylethylphenol detected in the cellulose acetate blank after chlorine exposure was also found with the FT-30 membrane both before and after exposure. One compound found in the cellulose acetate system blank after chlorine exposure, cyclohexanediol, was not found for the FT-30 membrane system, but one new compound, dibutylthiophene, was detected and identified after recirculating in the FT-30 system. In addition to the above substances, four unidentified compounds were detected in the FT-30 membrane chlorine exposure test, one of the four being present both before and after exposure.

The results of the leaching study for the two RO membranes are summarized by the following statements:

1. There appears to be little difference in leachables from the two RO membranes in the absence of chlorine.

2. Di-t-butylethylphenol was detected in the system blank of both RO membranes after chlorine exposure and for the FT-30 membrane before exposure to chlorine.

3. The coeluting peak at 15.2 minutes retention time are present in all samples and are probably not associated with the RO membranes but to other system components or a consistent extraneous contaminant.

4. In addition to the substances discussed in 2 and 3 above (di-t-butylethylphenol; di-t-butylbenzoquinone; and dimethylethylmethoxyphenol), there were two additional compounds identified for the cellulose acetate (cyclohexane-diol and butylbenzylphthalate) and four additional compounds (dibutylthiophene and three unknowns) for the FT-30 RO membranes (see Table 16).

5. None of the substances detected were obvious chlorination by-products.

6. Several of the compounds detected in the FT-30 membrane blank before and more obviously after chlorine exposure were nitrogen-containing compounds which may have originated from the barrier coating of the composite FT-30 membrane.

Two of the organic leachates identified in the RO system blanks (di-tert-butylethylphenol and butylbenzylphthalate, see Tables 15 and 16) have been found in similar leaching tests by Kopfler _et al._ (15) at the EPA Health Effects Research Laboratory.

The ion exchange membranes showed the only direct chlorination by-products observed in the leaching test. Several observations are evident from the data:

1. Few leachable compounds were apparent from the MA 3475 and Nafion^{R} membranes in the absence of chlorine.

2. Other than the coeluting peak at 15.2 minutes, only two compounds (benzaldehyde, and dichlorocyclohexane) were detected for the Nafion^{R} membrane after chlorination.

3. The largest number of additional compounds was detected for the MA 3475 membrane after chlorine exposure.

4. The identified leachables from the MA 3475 membrane can be grouped into three categories: a) compounds which are apparent chlorination by-products (chlorocyclohexane; dichlorocyclohexane; dichloronaphyridine; and five unknown chlorinated organics - see Table 18), b) phthalates, and c) the coeluting compounds dimethylethylmethoxyphenol and di-t-butylbenzoquinone, which were common to all samples.

5. The MA 3475 membrane appears to be the only membrane to show potentially significant increases in chlorinated methanes when exposed to chlorine.

The limited work done on leachables is encouraging since the number of organic substances apparently leaching from the membrane systems is few. Some concern must be expressed regarding the increase in number and type of compounds present when the systems, especially the MA 3475 membrane, are exposed to chlorine. Fortunately, the MA 3475 membrane is not normally used in field acquisition of samples, where the risk of exposure to significant chlorine levels is most likely.

d. Model Solute Recovery--

One of the most important factors in any sampling process is high overall recovery of as many different types of compounds as possible. Data from the concentration runs were initially examined for overall solute mass recovery wherever sufficient data were available. Table 36 lists the percent mass recoveries for the three concentration runs.

Equation 1 was used to calculate the percent recovery.

$$\text{Percent recovery} = (\text{final mass}/\text{initial mass})\ (100)$$

$$= [(C_f^F\ V_f^F)/(C_i^F\ V_i^F)]\ (100) \qquad (1)$$

Except where noted, initial and final masses were calculated using concentration data from Tables 30, 32, and 34 (Section 4.A.8) with an initial volume of 500 liters (132 gallons) and a final volume of 10 liters (2.6 gallons). Upon first inspection, the recovery values for many solutes appear low, especially for the cellulose acetate membrane. A more detailed analysis presented later indicates that under experimental conditions used, losses due to adsorption are considerable. Field application of this method should incorporate a conditioning period to satisfy the adsorptive demands of the system components. No corrections were made for adsorptive solute losses in Table 36, but estimates of these and other losses are provided later when system mass balances are determined, and corrected recoveries are calculated.

Two major comparisons can be made from the recovery data listed in Table 36. First, comparison of the recoveries of the cellulose acetate membrane (Run 618-41) and the FT-30 membrane (Run 618-51) readily shows that in essentially all cases, organic solute recovery by the FT-30 membrane equals or more often far exceeds the recovery demonstrated by the cellulose acetate membrane. This was not unexpected since membrane rejections determined for the two membranes in the screening tests and the concentration runs reflected this same trend. It will be shown later that data suggest that the general adsorptive solute losses for both RO membrane systems are about the same. It can then be inferred that better recoveries for the FT-30 membrane are apparently due to inherently better separation capabilities of the membrane (solute rejection).

TABLE 36. OVERALL RECOVERY DATA OBSERVED IN 50X CONCENTRATION RUNS (1)

	Cellulose Acetate no humics (Test Run 618-41)	FT-30 no humics (Test Run 618-51)	FT-30 with humics (Test Run 618-57)
isophorone	8.5	74	LA
2,4-dichlorophenol	1.3	54	52
quinoline	0.2†	19	12
1-chlorododecane	6.0	36	49
biphenyl	0.4	6.4	8.0
2,4-dichlorobiphenyl	--	--	0.7
2,2',5,5'-tetrachlorobiphenyl	0	5.2	16†*
2,6-di-tert-butyl-4-methylphenol	0.5†	4.6	2.0
caffeine	22	56	53
anthraquinone	0.7	8.4	5.0
stearic acid	--	--	3.2
bis(2-ethylhexyl)phthalate	--	--	5.2
5-chlorouracil	5.7†	66	45
furfural	--	6.8	--
glucose	24	24	16
glycine	--	--	--
chloroform	0.4	20	21
trimesic acid	--	--	--
methylisobutyl ketone	2.3	61	41
humic acid	--	--	54

(1) No corrections provided for solute losses due to adsorption

LA Lab accident (solute mistakenly not added)

† Initial masses are estimated from the amount of solute added to the system and not calculated from the analyzed solute concentration and initial volume

-- Insufficient data for calculation of recovery

* Final mass calculated assuming a 50-fold volume concentration and a constant rejection of the solute

e. Humic Acid Effects--

The second comparison available in Table 36 is between the FT-30 tests with (618-57) and without (618-51) humic acid in the water matrix. There are 12 pairs of data that can be compared directly. For comparison, three categories were defined: 1) higher recovery with humic acid present, 2) lower recovery with humic acid present, and 3) no difference. It was stipulated that the differences were to exceed 10 percent to qualify as significant.

The results of this comparison showed that higher recovery was exhibited for two compounds, 1-chlorododecane and 2,2'5,5'-tetrachlorobiphenyl, with humic acid present; and that lower recovery was exhibited for two compounds, 5-chlorouracil and methylisobutyl ketone, in the presence of humic acid. Most of the compounds (eight) showed no change when humic acid was present in the test matrix. These results should be viewed as preliminary indications since the errors at this level of analysis can be the limiting factor and the scope of this examination has to be considered limited.

The strongest and possibly the only general occurrence of a humic acid effect was observed in the screening evaluation of the Donnan membrane (Nafion^R). Table 37 lists percentages of the starting model solute mass found in the salt "pump" solution after the fixed period of Donnan treatment. Both the Nafion^R and MA 3475 membranes were tested without humic acid present, and the Nafion^R was retested with humic acid present. A measurable decrease in solute losses was demonstrated for nearly all solutes in the presence of humic acid, with most showing better than a 75% reduction in losses with humic acid present. Also evident from Table 37 is the measurably lower level of solute losses through the MA 3475 membrane than through the Nafion^R membrane.

Although the effect of humic acid was measurable in the screening test, the effect was not observed during the actual concentration test, as discussed earlier. This may be because the concentration test was conducted at a generally lower solute level than the screening test. Analytical errors are greater and solute adsorption can mask less obvious effects at these levels.

f. Membrane Model Solute Rejection--

Membrane rejection of organic solutes may be the single most important consideration in any membrane process used to recover organic materials from an aqueous stream. The importance of the rejection is evident when one examines the relationship between the expected batch recovery and the membrane rejection (equation 2)

$$\text{Mass recovery} = M_f/M_i = (C_f^F\ V_f^F)/(C_i^F\ V_i^F) = (V_i^F/V_f^F)^{R-1} \qquad (2)$$

where M_f and M_i are the final and initial solute masses respectively. The solute masses were calculated from the analytically determined initial and final solute concentrations (C_i^F and C_f^F) measured in the feed stream and the initial and final volume (V_i^F and V_i^F) of the feed solution. R equals the membrane solute rejection. Figure 15 shows the exponential relationship

TABLE 37. PERCENTAGE OF MODEL SOLUTE COMPOUNDS FOUND IN THE SALT STRIP SOLUTION BATH AFTER FOUR HOURS OF RECIRCULATION AND THE EFFECT OF MEMBRANE EXPOSURE TO HUMIC ACID

	Nafion^R hollow fiber membrane (Test Run 618-10) no humic acid	Nafion^R hollow fiber membrane (Test Run 618-48) humic acid in matrix	Ionac MA 3475 (Test Run 618-12) no humic acid
isophorone	10.9	3.2	<0.6
2,4-dichlorophenol	12.7	2.7	<0.1
quinoline	25.8	19.8	0
1-chlorododecane	34.6	<1.2	<1.4
biphenyl	13.4	3.4	<0.2
2,2',5,5'-tetrachlorobiphenyl	<10.1	2.1	18.2
2,6-di-tert-butyl-4-methylphenol	7.7	<0.2	<0.2
caffeine	--	4.2	<0.1
anthraquinone	12.1	0.2	<0.7
stearic acid	5.1	1.1	4.3
bis(2-ethylhexyl)phthalate	7.7	0.5	<0.9
furfural	89	14.3	<0.7
glycine	6.0	--	<0.6
chloroform	6.8	8.7	<0.7
methylisobutyl ketone	--	6.8	--

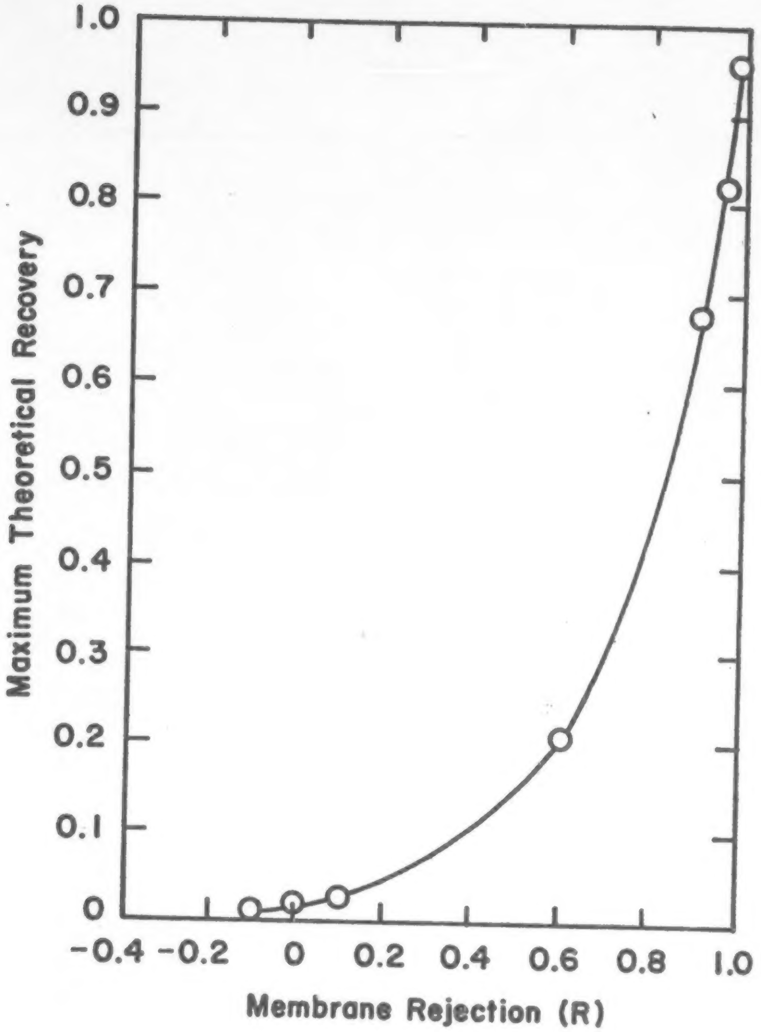

Figure 15. Theoretical mass recovery versus membrane rejection.

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between the expected recovery and membrane rejection. Organic rejection data was obtained from two series of tests during this study: the membrane screening (see Section 4.A.7) and the concentration runs (see Section 4.A.8).

The screening tests were routinely conducted at organic levels of 50X and salt levels of 5X to improve the accuracy of the determination. Analytical data from these tests were introduced in Tables 20-23, 27, and 28 (Sections 4.A.7). The membrane rejections were calculated using the classical rejection relation (equation 3) and the feed/permeate sample pairs from these tables.

$$\text{Rejection} \quad (R) = [1-(C^P/C^F)] \qquad (3)$$

Membrane rejection values from both the screening and concentration runs are presented in Table 38.

The first four columns list rejection values determined for the cellulose acetate membrane. Run numbers and the presence or absence of humic acid are also indicated. Similar data are presented for the FT-30 membrane in the sixth through tenth columns. A set of rejection values is also reported for the cellulose acetate and FT-30 concentration runs (618-41, 618-51, and 618-57). Each set represents determinations made at concentration factors of approximately 8X and 40X.

Several items in Table 38 require further explanation. First, negative rejection values are reported, particularly for the cellulose acetate membrane. This occurs any time the organic solute concentration is higher in the permeate stream than in the corresponding feed solution. Whenever this happens, equation 3 will yield negative values.

Examination of Table 38 will also reveal rejections listed as "<" or ">" values. This occurs through the use of analytical detection limits in the rejection calculation. Using this approach, a range of rejections can be defined even if an exact value cannot be calculated. A typical example is the isophorone rejection with the FT-30 membrane in run 618-09. Table 38 lists the rejection as ">90." This value wascalculated using equation 3 and the feed/permeate data analysis from Table 23 presented earlier. Table 23 lists a feed sample concentration of 1.3 mg/L and a permeate sample detection limit of <0.13 mg/L. The permeate value of <0.13 implies the concentration of isophorone is between 0 and 0.13 mg/L. The lowest rejection would result from a permeate concentration of 0.13; therefore, the rejection has to be greater than the value calculated using 0.13 mg/L in equation 3 (i.e., %R > 90).

Average rejections are listed in Table 38 in addition to the individual rejection values calculated from feed/permeate data pairs. The averages are calculated for each RO membrane from data in Table 38. Individual out-of-line values are not included in the averaging. Even though these averages are subject to many errors and assumptions, they serve as a general guide to the membrane's potential for retaining the solute and are

TABLE 38. SOLUTE REJECTION FOR THE CELLULOSE ACETATE AND FT-30 REVERSE OSMOSIS MEMBRANES FROM SCREENING AND CONCENTRATION RUNS

Model solutes	Percent Rejections*										
	CA (589-85) no humics	CA (618-04) no humics	CA (618-30) with humics	CA (618-41) no humics	CA average rejection	FT-30 (589-81) no humics	FT-30 (618-09) no humics	FT-30 (618-34) with humics	FT-30 (618-51) no humics	FT-30 (618-57) with humics	FT-30 average rejection
isophorone	68	73	97	74/61	(69)	>99	>90	>88	>91/99	--/>64	(96)
2,4-dichlorophenol	-158	-5	-20	-20/-57	(-52)	79	96	>98	91/96	98/94	(93)
quinoline	38	9	0	<0/>17	(16)	88	96	97	99/98	99/>99	(97)
1-chlorododecane	--	55	60	--/78	(64)	>57	>40	--	83/>96	>90/>96	(87)
biphenyl	-28	-8	-52	-31/-64	(-37)	88	>40	93	>95/>97	>96/--	(91)
2,2',5,5'-tetrachloro-biphenyl	--	--	<80	--/--	(--)	--	--	--	>38/23	--/>83	(46)
2,6-di-tert-butyl-4-methylphenol	38	94	72	>38/>62	(61)	>92	>91	>95	>83/>95	>90/>17	(96)
caffeine	9	78	73	67/67	(71)	>99	>99	>98	45/>99	98/99	(99)
anthraquinone	12	25	15	-11/-378	(10)	89	>80	>89	>98/87	>96/>90	(93)
stearic acid	33	>22	--	--/--	(--)	65	>43	--	--/--	--/>50	(71)
bis(2-ethylhexyl)-phthalate	64	--	--	--/--	(--)	54	--	--	>81/>88	>92/>88	(94)
trimesic acid	--	95	>90	--/--	(--)	--	93	>97	--/--	--/--	(96)
furfural	--	-90	-520	--/--	(--)	--	-26	--	61/36	>21/--	(53)
5-chlorouracil	--	40	46	32/44	(41)	--	97	71	>86/>97	>48/>95	(88)
glycine	--	97	--	--/--	(--)	--	>99	--	--/>7	>42/>71	(78)
glucose	--	--	--	96/96	(96)				99/99	99/99	(99)
chloroform	-123	-80	-210	-29/<-20	(-110)	22	84	88	>88/91	>88/90	(90)
methylisobutyl ketone				17/-20	(-1)				95/99	>99/99	(98)
humic acid	--	--	--	--/--	(--)	--	--	--	--/--	>92/>99	(98)

* All rejections indicated greater than (>) were obtained using the limit of detection in the analysis of the permeate sample. The actual rejection may approach 100

-- Cannot be determined from available data

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useful and necessary in the mass balance analysis of the data. Data which were incomplete or too scattered to provide reasonable estimates are indicated by "--" in Table 38.

g. Solute Adsorption--

Another important consideration in using a membrane system to concentrate organic solutes is determining to what magnitude solutes will be "taken up" or "lost from" the system. Initial work on the project suggested that solute volatility was a significant consideration for very few of the solutes (e.g., chloroform) and was not a prime consideration on the vast majority of those being used. The machanism implicated indirectly in the apparent disappearance of most of the solute materials was adsorption, even though limited solubility, biodegradation, and chemical decomposition of some solutes may be complicating factors. The losses of compounds have all been addressed under the classification of adsorptive losses for the empirical approach taken to the problem in this study.

Estimates of solute losses due to adsorption on the system components were provided by examination of the extent of material loss during the 4 hr of extended total solution recirculation. The data from all screening runs on the three membrane systems were examined with three primary comparisons in mind. First was to determine if any difference in the level of solute loss could be detected between identical membrane systems using test water with and without humic acid present in the matrix. The second comparison was to determine if differences could be seen in the level of adsorptive solute losses between the two different reverse osmosis membranes. The third objective of the solute loss comparisons was to determine if there was a difference between the solute losses with the reverse osmosis membranes and the solute losses with the Nafion^{R} membrane system.

Table 39 lists percent changes in solute levels occurring over the 4 hr period of total solution recirculation. The 4 hr recirculation period was designed into all screening tests for two reasons: 1) to provide a fixed period of equilibration before evaluating the membrane rejection and 2) to allow an estimate to be made of the solute losses occurring in the system due to adsorption, volatilization, solubility artifacts, or other as yet undefined phenomena. Negative values in Table 39 indicate a loss of solute material during the recirculation period. Positive values indicate apparent solute gains. When data was inadequate to estimate a solute level change, it was designated as "--" in Table 39. The "<" values listed reflect calculations of percent loss (or gain) involving analytical detection limits. For example, an initial sample with 0.06 mg/L and a final analysis of <0.05 mg/L would yield a minimum of 17 percent loss and as much as 100 percent if there were none of the solute in the sample collected at the end of the recirculation period. This technique accounts for the ranges shown in the column of averages.

An analysis of the data must include an awareness of the analytical demands on the program. The development of methods and the analysis of solutes at or near their limit of detection frequently provide results with a precision range of the same magnitude as the concentration level in the

TABLE 39. PERCENT SOLUTE ADSORPTION LOSSES (GAINS)

Model solutes	CA (589-85) no humics	CA (618-04) no humics	CA (618-30) with humics	FT-30 (618-09) no humics	FT-30 (589-81) no humics	FT-30 (618-34) with humics	Average loss
isophorone	-8.7	+29	+5.9	-35	0	-8.9	-2.9
2,4-dichlorophenol	-33	-27	-23	+29	-19	-14	-14.5
quinoline	-27	-22	-4.8	-39	-24	-6.3	-21
1-chlorododecane	>-75	-31	-64	-29	-84	>-17	-50 to -68
biphenyl	-73	-65	-74	-96	-83	-71	-77
2,2',5,5'-tetra-chlorobiphenyl	--	-50	>-50	>-63	--	-29	-48 to -70
2,6-di-tert-butyl-4-methylphenol	-46	--	-83	-73	-75	-71	-70
caffeine	--	0	-4.5	0	+4.7	-6.3	-1.2
anthraquinone	-47	-68	-32	-55	--	-73	-65
stearic acid	-36	-85	>-84	-74	-70	-70	-70 to -73
bis(2-ethylhexyl)-phthalate	-83	0-93	>-85	>-61	-84	-75	-80 to -90
trimesic acid	--	+9.5	-4.5	0	--	-11	-1.5
furfural	--	+203	-98	+213	--	--	(1)
5-chlorouracil	--	-3.8	-3.7	0	--	-4.8	-3.1
glycine	--	+19	--	+5.9	--	--	+12
chloroform	-24	-17	-68	0	-38	-35	-30

(1) Data too scattered to assess an average percent loss

-- Insufficient data to calculate values

+ Positive values suggest gains in solute levels during equilibration period.

sample. Calculation of rejection, adsorption, and recovery using these numbers leads to a relatively large uncertainty of the precision of the results. This problem, coupled with operational problems of performing the assays in the presence of high salt, acetone, and humic acid content, contributes to the apparent scatter of the resulting data. Despite these limitations, the data does indicate major changes or trends.

The first comparisons were done to evaluate screening runs for effect of humic acid in the matrix water on the solute losses to adsorption. Comparisons of the following solute compounds (isophorone; 2,4-dichlorophenol; quinoline; 1-chlorododecane; biphenyl; 2,2',5,5'-tetrachlorobiphenyl; 2,6-di-tert-butyl-4-methylphenol; caffeine; anthraquinone; stearic acid; bis(2-ethylhexyl)phthalate; and chloroform) revealed only four instances of an appreciable change in adsorptive solute loss for a membrane tested on water matrices with and without humic acid. None of the four changes were greater than 50 percent. Considering the magnitude of the scatter in data, these changes may not be significant.

With the cellulose acetate membrane system two compounds showed a possible effect with humic acid. The system adsorption solute loss of 2,6-di-tert-butyl-4-methylphenol went from 46 percent to 83 percent, and chloroform went from 24 percent to 68 percent in the experiments incorporating humic acid in the matrix. These changes, particularly values associated with chloroform, may not be related to the presence of humic materials but relate to volatility and other properties of the solute. With the FT-30 reverse osmosis membrane system, only one compound, 2,2'5,5'-tetrachlorobiphenyl, demonstrated an effect with humic acid present. The change in tetrachlorobiphenyl was improved in this case by going from a 63 percent adsorption to a 29 percent loss in the presence of humic acid. The fourth compound to show a possible change was quinoline, which changed from a loss of 28 percent to 74 percent with the presence of humic acid on the Nafion^{R} membrane screening. However, these changes are isolated and based upon a limited data base. They do not represent a strong trend showing any uniform change of adsorption with humic acid in the test water matrix.

The second objective of the comparisons of adsorptive solute losses was to determine whether significant differences exist between the two reverse osmosis systems both with and without the presence of humic acid. No significant differences in solute losses were found between the two reverse osmosis membrane systems. The demonstrated differences of solute rejection and the totally different composition (adsorptive properties) between the two membranes would tend to indicate that primary adsorptive losses may be occurring on or possibly predominated by components of the system other than the active membrane material itself. This would tend to explain why the significant adsorptive losses in both RO systems are very similar.

The third and final comparison which was evaluated was between the adsorptive losses of the reverse osmosis membrane systems and those of the Nafion^{R} membrane system. In this comparison, less adsorption was found in the Nafion^{R} system than with the reverse osmosis loops. This may be due in part, to the reduced area of the Nafion^R membrane as compared to that of the RO membranes. It could also be due to the inherently more inert chemical structure of the Nafion^R type membrane as compared to the RO membranes.

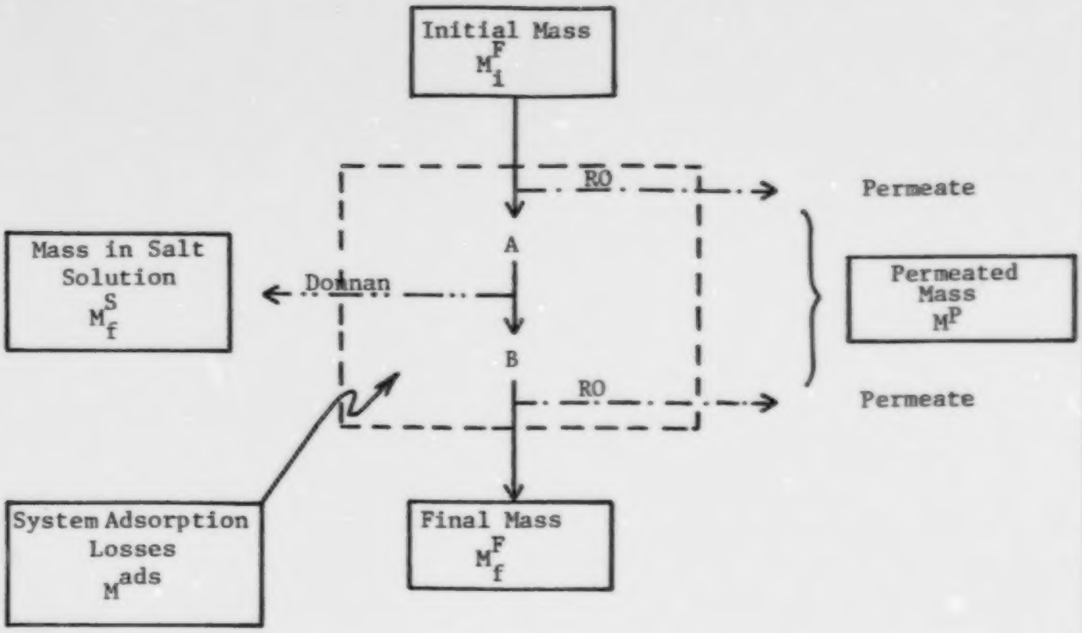
On the whole, several model solute compounds exhibited significant losses to mechanisms other than membrane permeation. Included among the solutes showing losses in excess of 50 percent are bis(2-ethylhexyl)phthalate; stearic acid; anthraquinone; 2,6-di-tert-butyl-4-methylphenol; biphenyl; and chlorododecane. These adsorption mechanisms are probably reversible and account for the occasional presence of these compounds in system blank analyses and for an absence of a "demand-satisfaction" effect (i.e., a decrease in adsorption of solutes due to satisfaction of the demand for them by repeated exposures of the membrane to the organic model solutes). At the loading levels designed in this program, the adsorption of solute may be the predominant factor influencing the recoveries of some solutes. This aspect was investigated further when the solute adsorption data was used to aid in evaluating system mass balances for the concentration test runs.

h. Mass Balance Calculations--

Mass balance evaluations were performed for all three concentration runs where analytical data was available to complete calculations. Figure 16 illustrates the five major components into which the system was divided for the mass balance determination. These components include initial and final feed (concentrate) solutions, as well as components that permeated the reverse osmosis membrane, components in the salt solution that permeated the Donnan membrane, and mass loss to adsorption. General formulas used for calculating each of the masses are also shown in Figure 16. Tables 40, 41 and 42 include the results of these calculations for each of the three concentration runs.

The calculation of initial mass (M_i^F) in the system is straightforward and involves only the initial solute concentration (C_i^F) and the initial solution volume (V_i^F). The final mass (M_f^F) was calculated as was the initial mass, except that the final measured solute concentration (C_f^F) and final measured volume (V_f^F) were used. The mass of solute in the salt solution (M_f^S) was estimated from the measured concentration (C_f^S) and volume (V_f^S) of the salt solution. Calculation of the masses lost to adsorption (M^{ads}) and everse osmosis membrane permeation (M^P) are discussed below. Ideally, the sum of all the parts ($M_f^F + M_f^S + M^P + M^{ads}$) should equal the whole, or initial mass (M_i^F).

The mass loss to reverse osmosis membrane permeation (M^P) is difficult to assess directly, due to the typically low solute concentration in this stream. These concentrations routinely were a factor of 10 or more below the original solution and in the majority of samples were well below the analytical detection limits. Because of increased uncertainty in the analytical data as the detection limit is approached and absence of data for many solutes, an estimate of the losses experienced in permeation was obtained using equation 4 first to calculate a projected final solute


Initial Mass M_i^F
RO
Permeate
A
Mass in Salt Solution M_f^S
Donnan
Permeated Mass M^P
B
RO
Permeate
System Adsorption Losses M^{ads}
Final Mass M_f^F

$$\underline{M_i^F = M_f^F + M_f^S + M^P + M^{ads}}$$

Initial Mass = $M_i^F = (C_i^F)(V_i^F)$

Final Mass = $M_f^F = (C_f^F)(V_f^F)$

Mass in Salt Solution = $M_f^S = (C_f^S)(V_f^S)$

System Adsorption Losses = $M^{ads} = (\bar{\%})(C_i^F)(V_i^F)$

Permeated Mass = $M^P = \left[\begin{array}{l}\text{Final Mass Expected}\\ \text{With 100\% Recovery}\end{array}\right] - \left[\begin{array}{l}\text{Final Mass Predicted using}\\ \text{a Fixed Membrane Rejection}\end{array}\right]$

$$= (C_i^F)(V_i^F) - (\bar{C}_f^F)(V_f^F)$$

$$= M_i^F - (\bar{C}_f^F)(V_f^F)$$

$$\text{with } \bar{C}_f^F = (C_i^F)(V_i^F/V_f^F)^R$$

* See text section 4.A.9.h for further description of these terms.

Figure 16. Component streams used in determing system mass balances.

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TABLE 40. MASS BALANCE DATA AND ESTIMATES OF SOLUTE RECOVERY (1) (TEST RUN 618-41). CELLULOSE ACETATE MEMBRANE CONCENTRATION WITHOUT HUMICS

	M_i^F	M_f^F	M^{ads}	M^P	M_f^S	Sum $M_f^F+M^{ads}+M^P+M_f^S$	Percent mass accountable	M_i^F	Total % recovery
isophorone	26	2.2	0.8	18.3	0.08	21.3	82	25.2	8.7
2,4-dichlorophenol	15	0.2	2.3	15	0.09	17.6	117	12.7	1.6
quinoline	25**	0.05	5.3	24.1	0.05	29.5	118	19.7	0.3
1-chlorododecane	5	0.3	2.5-3.4*	3.8	<0.05	6.6-7.5	132-150	1.6-2.5	12-19
biphenyl	21.5	0.09	16.6	20.5	<0.05	37.2	173	4.9	1.8
2,4-dichlorobiphenyl	#	#	#	#	#	#	#	#	#
2,2',5,5'-tetrachlorobiphenyl	2.5	ND	1.2-1.8*	2.5†	ND	3.7-4.3	148-172	0.7-1.3	0
2,6-di-tert-butyl-4-methylphenol	24**	0.12	16.8	18.8	<0.05	35.7	149	7.2	1.7
stearic acid	#	#	#	#	#	#	#	#	#
caffeine	27.5	6.1	0.3	22.2	0.3	28.9	105	27.2	22
bis(2-ethylhexyl)phthalate	#	#	#	#	#	#	#	#	#
anthraquinone	28	0.2	18.2	27.2	<0.05	45.6	163	0.8	25
furfural	#	#	#	#	#	#	#	#	#
5-chlorouracil	28**	1.6	0.8	25.2	<0.5	27.6-28.1	99-100	27.2	5.9
glycine	#	#	#	#	#	#	#	#	#
glucose	20	4.8	1.0***	3.0	0.1	8.9	45	19	25
trimesic acid	#	#	#	#	#	#	#	#	#
chloroform	24	0.1	7.2	24	<0.1	31.4	131	16.8	0.6
methylisobutyl ketone	22	0.5	4.4***	21.6	0.1	26.6	121	17.6	2.8

* Ranges of data. Result from percentage adsorption loss ranges such as the range -50 to -68 percent for 1-chlorododecane as seen in Table 39

** Initial masses are estimated from the amount of solute added to the system and not calculated from the analyzed solute concentration and initial volume

*** Due to limited data to calculate adsorptive loss percentages, values have been assumed based primarily upon solute water solubility and secondly upon solute volatility (e.g., glucose = 5% and methyliscbutyl ketone = -20%)

† Mass calculated assuming a 50-fold volume concentration and an assumed constant rejection of the solute

(1) Correction for losses to adsorption have been factored into calculations of overall solute recovery

# Insufficient data to complete mass balance calculations

TABLE 41. MASS BALANCE DATA AND ESTIMATES OF SOLUTE RECOVERY (1) (TEST RUN 618-51). FT-30 MEMBRANE CONCENTRATION WITHOUT HUMICS

	M_i^F	M_f^F	M^{ads}	M^P	M_f^S	Sum $M_f^F+M^{ads}+M^P+M_f^S$	Percent mass accountable	$\hat{M}_i^F$	Total % recovery
isophorone	25	18.6	0.8	6.0	1.3	26.7	107	24.2	77
2,4-dichlorophenol	20	10.7	2.9	3.0	0.5	17.1	86	17.1	63
quinoline	25	4.8	5.3	1.0	1.3	12.4	50	19.7	24
1-chlorododecane	4.5	1.6	2.3-3.1*	0.7	<0.05	4.6-5.4	102-120	1.4-2.2	73-114
2,4-dichlorobiphenyl	#	#	#	#	#	#	#	#	#
biphenyl	25	1.6	19.3	4.0	0.2	25.1	100	5.7	28
2,2',5,5'-tetrachlorobiphenyl	#	#	#	#	#	#	#	#	#
2,6-di-tert-butyl-4-methylphenol	24**	1.1	16.8	8.4	.32	26.6	111	7.2	15
stearic acid	#	#	#	#	#	#	#	#	#
caffeine	25	13.9	0.3	1.0	1.1	16.3	65	24.7	56
bis(2-ethylhexyl)phthalate	#	#	#	#	#	#	#	#	#
anthraquinone	25	2.1	16.3	8	0.2	26.6	111	8.7	24
furfural	#	#	#	#	#	#	#	#	#
5-chlorouracil	34**	22.5	1.0	13	1.5	38	112	33	68
glycine	#	#	#	#	#	#	#	#	#
glucose	18	4.4	0.9***	1.0	0.2	6.4	36	17.1	26
trimesic acid	#	#	#	#	#	#	#	#	#
chloroform	22.5	4.6	6.8	8.5	0.7	20.6	92	15.7	29
methylisobutyl ketone	20	12.1	4.0***	2.9	1.3	20.3	102	16	76

* Ranges of data. Result from percentage adsorption loss ranges such as the range -50 to -68 percent for 1-chlorododecane as seen in Table 39

** Initial masses are estimated from the amount of solute added to the system and not calculated from the analyzed solute concentration and initial volume

*** Due to limited data to calculate adsorptive loss percentages, values have been assumed based primarily upon solute water solubility and secondly upon solute volatility (e.g., glucose = -5% and methylisobutyl ketone = -20%)

(1) Corrections for losses to adsorption have been factored into calculations of overall solute recovery

Insufficient data to complete mass balance calculations.

TABLE 42. MASS BALANCE DATA AND ESTIMATES OF SOLUTE RECOVERY (1) (TEST RUN 618-57). FT-30 MEMBRANE CONCENTRATION WITH HUMICS PRESENT

	M^F	M_f^F	M^{ads}	M^P	M_f^S	Sum $M_f^F+M^{ads}+M^P+M_f^S$	Percent mass accountable	R_i^F	Total % recovery
isophorone	...compound not added - lab accident...								
2,4-dichlorophenol	20	10.3	3	3	0.4	16.7	84	17	61
quinoline	30	3.6	6.3	3	0.1	13	43	23.7	15
1-chlorododecane	3.5	1.7	1.8-2.4*	0.8	<0.05	4.3-4.9	123-140	1.1-1.7	100-154
biphenyl	15	1.2	11.6	2.7	0.1	15.6	104	3.4	35
2,4-dichlorobiphenyl	#	#	#	#	#	#	#	#	#
2,2',5,5'-tetrachlorobiphenyl	1.5**	.24†	0.7-1.1*	1.2	<0.05	2.1-2.5	140-167	0.4-0.8	30-60
2,6-di-tert-butyl-4-methylphenol	5	0.1	3.5	1.6	<0.05	5.2	104	1.5	6.7
caffeine	30	16	0.4	2.0	1.1	19.5	65	29.6	54
anthraquinone	30	1.5	19.5	7.0	0.2	28.2	94	10.5	14
bis(2-ethylhexyl)phthalate	#	#	#	#	#	#	#	#	#
stearic acid	28	0.9	19.6	22.6	<0.3	43	155	8.4	11
5-chlorouracil	27	12.1	0.8	10	0.8	23.7	88	26.2	46
furfural	#	#	#	#	#	#	#	#	#
glucose	26	4.2	1.3***	2.0	0.2	7.7	30	24.7	17
glycine	#	#	#	#	#	#	#	#	#
chloroform	22	4.6	6.6	8	0.7	19.9	90	15.4	30
trimesic acid	#	#	#	#	#	#	#	#	#
methylisobutyl ketone	21	8.6	4.2***	2.0	1.3	16.1	77	16.8	51
humic acid	900	486	45	72	28	631	70	855	57

* Ranges of data. Result from percentage adsorption loss ranges such as the range -50 to -68 percent for 1-chlorododecane as seen in Table 39

** Initial masses are estimated from the amount of solute added to the system and not calculated from the analyzed solute concentration and initial volume

*** Due to limited data to calculate adsorptive loss percentages, values have been assumed based primarly upon solute water solubility and secondly upon solute volatility (e.g., glucose = 5% and methylisobutyl keytone = -20%)

† Mass calculated assuming a 50 fold volume concentration and an assumed constant rejection of the solute

(1) Correction for losses to adsorption have been factored into calculations of overall solute recovery

Insuffieicnt data to complete mass balance calculations.

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concentration ($\bar{C}_f^F$) knowing the initial concentration, initial volume, final volume, and membrane rejection (from Table 38) for the model solutes. The mass loss to permeation through the RO membrane was then calculated by using this projected final concentration and the final volume to estimate a final solute mass predicated on experimentally determined solute rejections and subtracting this from the total amount of spiked material available for recovery. These equations have been shown to predict the experimental changes in permeate concentration as a function of time and feed concentration (16)

$$\bar{C}_f^F = C_i^F(V_i/V_f)^R \tag{4}$$

The mass loss to permeation data as reported assumes a constant membrane rejection and has not been adjusted for adsorption losses. These factors may contribute to an apparent recovery of greater than 100 percent.

The last mass term calculated in Tables 40-42 is a measure of the mass of material adsorbed in the system. The estimation of adsorption losses is based primarily on adsorptive loss experienced over a 4 hr period where the system was set up on total recycle. Table 39 provided a tabulation of these calculated percent solute losses experienced in earlier test runs. Although there is considerable scatter in the data, the average loss value (%) should provide a workable estimate of losses where the number of measurements in the averaging was statistically significant. The average adsorptive percentage loss was then multiplied by the initial solute mass (initial solute concentration times the initial solution volume) to calculate the estimated adsorptive mass loss (M^{ads}) figures listed in Tables 40-42.

The "percent mass accountable" column provides a measure of how well the sum of the parts equals the whole. Better than 70 percent of all calculated values fall within a mass accountable range of 100 percent ± 50 percent. This appears to be a reasonable expectation considering all the factors influencing this calculation and the scatter and reliability of the data. One solute that is consistently and noticeably not well accounted for in the mass balances is glucose. This may be due to adsorption and/or biological degradation.

The last two columns of Tables 40-42 are used to evaluate the overall recovery of solute through the concentration process when corrections are made for losses to adsorption. The total percent recovery is calculated using the final mass recovered (M_f^F) and the corrected mass available ($\hat{M}_i^F$). The total percent recovery is calculated using equation 5.

$$\text{Total percent recovery} = [(M_f^F)/(\hat{M}_i^F)]\ (100) \tag{5}$$

The corrected mass available ($\hat{M}_i^F$) differs from initial mass in the system (M_i^F) in that adjustment is made for the adsorptive loss component (M^{ads}). The rationale for this approach is that in the field collection of samples the system would be preconditioned with source water prior to actual collection of samples in an attempt to satisfy the adsorptive demands of the system. Under these conditions it is anticipated that total percent recoveries calculated in Tables 40-42 would be more realistic than those calculated in the more conventional manner which were presented earlier in Table 36. By comparing the recovery values in Tables 40-42 with those in Table 36, it is apparent that for the most part there are small differences between values for compounds where relative adsorption losses are small and significantly larger differences for compounds with large adsorptive loss components.

Lead was added to the test water matrix to attempt to monitor the buildup of toxic metals during the concentration process. The lead was added as lead nitrate, and initial target levels were 20 µg/L. The concentrations of lead were determined by atomic absorption spectroscopy, and results are listed in Tables 32-35 for the two concentration runs where lead was monitored (618-51 and 618-57). The masses of lead were calculated at various times in the main process solutions (see Figure 3 for target sampling regime) to provide an assessment of the distribution of lead ions during the concentration. The result of these calculations are presented in Table 43. The mass of lead in concentrate and salt "pump" solutions (M^{S+P}) is also expressed as a percent of the original spiked mass. An estimate of the mass of lead lost due to RO permeation (assuming a constant 75 percent lead rejection) is provided, and the total mass of all three streams (M^{S+F+P}) is reevaluated as a percentage of original mass present. Each line entry in Table 43 represents the lead distribution in the operating concentration system at distinct events in the process (at 8X concentration factor; the end of the Donnan softening, 12·7X; at 40X and 50X concentration factors).

Several observations can be made from the data in Table 43. the lead concentration in the concentrate solution increases (by a factor of 5-10 times starting levels) during the 50-fold volumetric concentration. Donnan softening reduces levels of lead in the concentrate but not at the rate experienced for calcium ion in earlier studies. The mass of lead distributed between the concentrate and salt pump solution account for approximately 70 percent of the initial lead charge, and the balance, 30-40 percent, is lost in the permeate stream during the first 437 liters (115 gallons) processed by RO. A rejection of .75 for lead was selected for the mass balance estimate based in part upon the average values reported in Tables 33 and 35 and the experience of the authors. Scatter in the lead rejection data and the overall low values measured could not be explained with the limited data available. The constant rejection of lead at 75 percent should be corrected for concentration effects (lower rejections are often experienced with increaseing salt burdens), and this may account for the total mass (M^{S+F+P}) exceeding 100 percent in the later stages of concentration. The reason for the decrease of lead levels in the final concentration stages (40X to 50X) cannot be concluded from the available information.

i. Organic Solute Mass Recoveries

Table 44 presents the organic concentration factors achieved in the RO

TABLE 43. LEAD MASS BALANCE DATA (1)

CF	F(mg/L)	M^F(mg)	M^S(mg)	M^{S+F}(mg)	% of original	M^P(mg)	M^{S+F+P}(mg)	% of original
Concentration run without humic acid (Run No. 618-51) R = 0.75 for lead								
1X	0.012	6.00	-	6.0	100	-	6.0	100
8X	0.057	3.56	-	3.56	59	2.43	5.99	100
12.7X	0.028	1.09	3.75	4.84	81	2.85	7.69	128
40X	0.083	1.04	3.75	4.79	80	3.61	8.40	135
50X	0.065	0.65	3.75	4.40	73	3.74	8.10	135
Concentration run with humic acid (Run No. 618-57) R = 0.75 for lead								
1X	.024	12	-	12.0	100	-	12.0	100
8X	.134	8.38	-	8.38	70	4.86	13.24	110
12.7X	.054	2.11	5.57	7.68	64	5.5	13.18	110
40X	.264	3.30	5.57	8.87	74	7.23	16.10	134
50X	.220	2.20	5.57	7.77	64	7.49	15.3	128

F_F- feed sample lead concentration.
M_s - calculated mass in remaining feed (concentrate) solution.
M_P - mass of lead determined in the salt strip solution.
M - estimated mass of lead permeated.
(1)- initial volume of feed solution = 500L.
CF - volumetric concentration factor

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TABLE 44. THEORETICAL (1) AND ACTUAL CONCENTRATION FACTORS (CF) EXPERIENCED IN LABORATORY CONCENTRATION TEST (50X VOLUMETRIC)

Model solute	Cellulose acetate (Run 618-41)		FT-30 (Run 618-51)		FT-30 (Run 618-57)	
	CF (theoretical)	CF (actual)	CF (theoretical)	CF (actual)	CF (theoretical)	CF (actual)
isophorone	14.9	4.2	43	37	43	--
2,4-dichlorophenol	~1	<1	38	27	38	26
quinoline	1.9	<1	45	9.6	45	6
1-chlorododecane	12.2	2.5	30	17.8	30	24
biphenyl	~1	<1	35	3.2	35	4
2,6-di-tert-butyl-4-methylphenol	10.8	1.7	43	2.2*	43	1
caffeine	16.1	11.1	48	28	48	27
anthraquinone	1.5	<1	38	4.2	38	2.5
stearic acid	--	--	16	--	16	1.6
5-chlorouracil	--	3.2*	32	45*	32	22
glucose	42.7	11.9	48	12.2	48	8.1
chloroform	~1	<1	34	10.2	34	10.5
methylisobutyl ketone	~1	1.2	46	30.3	46	20.4

*Calculated assuming target concentration of solute was spiked

--Insufficient data to calculate value.

(1) maximum predicted concentration factor predicted assuming a constant organic rejection as listed in Table 38.

concentration test. The "actual values listed in Table 44 are calculated as ratios of the final to initial concentrations of solutes that were listed earlier in Tables 30, 32, and 34. The "theoretical" maximum concentration factors are calculated using equation 4 to determine a predicted final concentration which incorporates the permeation losses and then dividing the predicted final concentration by the initial concentration.

The improved performance of the FT-30 membrane is again evident from these data. Several solutes that exhibited high adsorption losses throughout the study showed lower concentration factors (<5). But sill, more than half of the compounds attained better than 10X concentration factors. The poor performance of the cellulose acetate membrane may be attributed to the presence of acetone in the test matrix.

Table 45 lists model solute mass recoveries for each class of organic solute included in the concentration experiments. Table 45 lists actual and theoretical maximum (after accounting for solute lost through permeation) recoveries for both cellulose acetate and FT-30 membranes. The actual percent recoveries listed are from test runs 618-41, 618-51 and 618-57 for the cellulose acetate (without humic present), FT-30 (without humic present) and FT-30 membrane (with humic present) concentration test respectively. The theoretical maximum recovery is calculated from equation 2 (presented earlier) and membrane solute rejections listed in Table 38. Unfortunately, many of the recoveries could not be calculated because of insufficient data.

Several observations can be made from examining the data in Table 45: a) recoveries for the FT-30 membrane are without exception better than those experienced with the cellulose acetate membrane. In most cases the FT-30 membrane recoveries far exceeded those of the cellulose acetate membrane b) Several compounds (humic acid, caffeine, 5-chlorouracil, isophorone, MIBK, 2,4-dichlorophenol) were recovered at greater than 50 percent using the FT-30 membrane. On the other hand, no solute was recovered at greater than 24% with the cellulose acetate membrane. c) Several compounds (furfural, 2,4-dichlorophenol, biphenyl and chloroform) exhibited negative rejections with the cellulose acetate membrane. There was only one instance (furfural) where a negative rejection was observed with the FT-30 membrane and it was not observed consistently. d) Neither membrane demonstrated solute recoveries at levels approaching the anticipated maximums. Compounds which demonstrated higher levels of adsorption (biphenyl, chlorobiphenyls, anthraquinone, stearic acid, phthalate) were less efficiently recovered than compounds exhibiting lower levels of adsorptive losses. It may well be that some of this adsorptive capacity of the concentration system can be satisfied by exposure of the system components to the sample being concentrated. This is drawn upon field experience and TOC analysis which demonstrate higher recoveries for the system in actual use. More study into this area is needed to acquire a better definition of this phenomenon.

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TABLE 45. MODEL SOLUTE MASS RECOVERIES EXPERIENCED IN A 50X CONCENTRATION

Class	Compound	Cellulose Acetate		FT-30		
		Actual	Maximum†	Actual w/o Humic	Actual with Humic	Maximum
Acids	Trimesic acid	**	76	**	**	86
	Stearic acid	**	>6	**	3.2	86
	Humic acid	*	*	*	54	92
	Glycine	**	89	**	**	42
Aldehydes	Furfural	**	~0	6.8	**	16
Amines	Quinoline	0.2	3.7	19	12	89
	Caffeine	22	32	56	53	96
	5-Chlorouracil	5.7	10	66	45	63
Carbohydrates	Glucose	24	86	24	16	96
Chlorobiphenyls	2,4-Dichlorobiphenyl	**	**	**	0.7	**
	2,2'5,5'-Tetrachlorobiphenyl	0	**	5.2	16	12
Esters	Bis(2-ethyloxy)phthalate	**	**	**	5.2	79
Hydrocarbons	1-Chlorododecane	6.0	24	36	49	60
	Biphenyl	0.4	~0	6.4	8.0	70
Ketones	Isophorone	8.5	30	74	LA	86
	Anthraquinone	0.7	3	8.4	5.0	76
	Methylisobutylketone	2.3	~0	61	41	92
Phenols	2,4-dichlorophenol	1.3	~0	54	52	76
	2,6-Ditert-butyl-4-methylphenol	0.5	22	4.6	2.0	86
Trihalomethanes	Chloroform	0.4	~0	20	21	67

* Not present in test matrix ** Insufficient data to calculate a value
† Theoretical maximum recovery based on calculations using equation (2) LA - Lab accident

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B. ANALYTICAL CHEMISTRY

The analytical chemistry task of this study has been presented as a distinct task primarily for two reasons. First, the separation of the analytical task and the membrane evaluation task provides a clear presentation of the membrane evaluation data. Second, the magnitude of the analytical challenge itself suggested separate handling. Although the analytical chemistry task was to be a support function for the membrane evaluation, it quickly became apparent that analysis of the variety of compounds, the trace levels required, and the varying matrices of the samples would be a major technical challenge in the program.

Many of the standard analytical procedures referenced in this section evolved through one or more modifications devised to improve accuracy, precision, and freedom from interferences. Although additional efforts would have been devoted to analytical method development and method refinement, time, cost limitations, and the need to retain perspective of primary project objectives required restrictions to method development in some areas. Some points of interest and recurring problem areas are discussed below.

1. Model Organic Solutes

The original list of model solutes which were targeted for use in this study included 23 compounds distributed among 11 major chemical classes. Many of these compounds presented few analytical problems. Others, such as quinaldic acid, crotonaldehyde, and benzo(e)pyrene, eluded adequate method development during the study. Difficulties such as instability, limited detection levels, background interference, and cost and time restrictions were major factors.

Efforts in method development continued throughout the study to improve recoveries, improve precision and accuracy, and confirm methods for the more difficult compounds. Membrane evaluations were initiated prior to confirmation of methods for some of the compounds. This was necessary to keep membrane test schedules intact. Therefore, many early test evaluations did not include all model solutes.

Table 46 shows the original list of model solutes along with the solutes for which methodologies were established and confirmed. SOPs for analytical methods for each solute are also referenced in Table 46.

2. Detection Limits

The quantitative detection limits for each of the model organic solutes are specified in Appendices G through N. Analytical responses have been shown to be linear down to the specified lower limits. Results listed as not detectable (ND) in data tables indicate that the analysis showed the compounds were not present or were well below the linear response region.

Some analytical results, particularly from test series such as those evaluating the effects of chlorine exposure, indicate values lower than the linear detection thresholds. Data such as this occur due to detection of model solutes at levels above the "absolute" detection limit but well below the linear limit. However, it was felt that due to the nature of the test series and objectives, these values could be significant and should be reported. Errors and data scatter will be significantly greater at these levels than results determined to be within the well characterized linear detection range.

No effort was made to determine absolute detection limits since they vary from sample to sample and day to day depending upon matrices and instrumental conditions.

3. Inorganic Salts

Inorganic salts presented the most significant problem encountered routinely throughout the study. The samples generated from membrane evaluation studies contained varying levels of mixed inorganic salts ($CaSO_4$ + $CaCl_2$ + $NaHCO_3$). Salt levels in samples collected during the secondary screening test ranged from approximately 1200 mg/L total dissolved solids (TDS) for "system blank" samples to 58,000 mg/L (1 M) for the Donnan "pump" solution samples. Samples collected during the concentration test included an even wider range of salts (200 to 58,000 mg/L).

It was beyond the scope of this study to examine the effects of the variety and range of salts on the analysis of 20 different solutes, but gross adverse effects were observed and noted. some methods had to be modified to handle the high salt samples. Methods involving solvent extraction into an organic phase prior to analysis (Groups 1 and 2, Appendices G and H) and radiotracer methods (Appendix J) were apparently not affected. On the other hand, the HPLC methods developed for trimesic acid, furfural, glycine, and 5-chlorouracil could not tolerate samples with salts at a concentration greater than 100 ppm. The original HPLC methods were based on reverse phase separation by a C18 column. High salt samples destroyed the C18 column. To solve this problem, an HPLC method based on size exclusion an dliquid partition was developed using an Aminex HPX-85 column. This column could tolerate up to 1 M salts by simply cleaning the column when necessary. With this method, furfural, 5-chlorouracil, and humic acids could be analyzed.

4. Acetone

In many of the samples generated from the RO system, acetone was present at much higher concentrations than the compounds of interest. The HPLC methods for furfural, trimesic acid, and 5-chlorouracil use UV detection. Acetone exhibits strong UV absorbance at the same wavelengths that are optimum for these compounds. Therefore, much time was devoted to determining the parameters needed to achieve and maintain necessary column resolution. The salts compounded this problem, because a slight decrease in column resolution caused by the salts would be insignificant were it not for the presence of acetone in the sample.

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TABLE 46. MODEL SOLUTES AND ANALYTICAL SOP USED IN THE REVERSE OSMOSIS MEMBRANE EVALUATION STUDY

Original target model solutes	Chemical class	Model solutes with confirmed methodologies	SOP (Appendix)
quinaldic acid	Acids	-	-
trimesic acid		trimesic acid	K
stearic acid		stearic acid	G
humic acid		humic acid	N
glycine		glycine	I
furfural	Aldehydes	furfural	L
crotonaldehyde		-	-
quinoline	Amines	quinoline	G
caffeine		caffeine	G
5-chlorouracil		5-chlorouracil	M
glucose	Carbohydrates	glucose	J
2,4'-dichlorobiphenyl	Chlorobiphenyls	2,4'-dichlorobiphenyl	G
2,2',5,5'-tetrachlorobiphenyl		2,2'5,5-tetrachlorobiphenyl	G
bis(2-ethylhexyl)phthlate	Esters	bis(2-ethylhexyl)phthlate	G
1-chlorododecane	Hydrocarbons	1-chlorododecane	G
biphenyl		biphenyl	G
isophorone	Ketones	isophorone	G
anthraquinone		anthraquinone	G
methyl isobutyl ketone		methyl isobutyl ketone	G
2,4-dichlorophenol	Phenols	2,4-dichlorophenol	G
2,6-di-tert-butyl-4-methylphenol		2,6-di-tert-butyl-4-methylphenol	G
benzo(e)pyrene	Polynuclear aromatic hydrocarbons	-	-
chloroform	Trihalomethanes	chloroform	H

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APPENDIX A

STANDARD OPERATNG PROCEDURE FOR REVERSE OSMOSIS MEMBRANE/ORGANIC SOLUTE RETENTION SCREENING

A. Flush Procedure

Flushing of the system is accomplished by completing the following four operations. If samples are collected during the flush sequence, they will be designated with a Roman numeral "I" and assigned a subscript to designate the time (in hours) the sample is collected in the sequence and a superscript to designate whether the sample is a feed (F) or permeate (P) sample. Later nomenclatures were shortened to simply a letter (F,P) to indicate whether the sample was collected from the recirculating feed (F) solution or the permeate (P) stream and a numerical value indicating time elapsed (in hours - hrs) from the beginning of the test phase to the time of sampling.

1. Install the study reverse osmosis (RO) membrane flush.

2. Flush the RO system with two changes (25 gallon/change) of organic free water (OFW) for 3 hours each with permeate to waste. The volume concentration factor (CF) should not exceed five.

3. Next, flush the RO system with four 9 gallon changes of 5X inorganic matrix water (30 minutes each). Operate with permeate to reservoir and no overall increase in concentration factor.

4. Finally, flush the RO system with a single, 9 gallon batch of 5X inorganic matrix water and flush both permeate and reject flows to waste.

B. System Blank

The system blank is determined by analyzing an inorganic matrix water sample before and after an extended period of recirculation in contact with the membrane system. Blank samples are designated with a Roman numeral "II." Superscript and subscripts are assigned (as for flushing samples above) to reflect sample collection time and source stream. Later nomenclatures were shortened to simply a letter (F,P) to indicate whether the sample was collected from the recirculating feed (F) solution or the permeate (P) stream and a numerical value indicating time elapsed (in hours - hrs) from the beginning of the test phase to the time of sampling.

1. Recirculate a batch (9 or 7* gallons) of 5X inorganic matrix water

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*A 7 gallon volume is used when glycine and 5-chlorouracil are being spiked in part C.

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with both permeate and reject streams returning to the process drum. Sample the feed after 5 minutes' recirculation.

2. Maintain the solution temperature at 20 ± 1°C by control of coolant flow through cooling coils. Keep system covered.

3. Continue to recirculate the 5X inorganic matrix water for 4 hours and resample the feed. Turn the RO system off temporarily.

C. Membrane Solute Screening

The retention of specific organic compounds by the reverse osmosis membranes is determined by measuring the concentration of selected compounds in both feed and permeate streams after a period of operation to allow the system to equilibrate. The following steps are designed to accomplish this objective. Solute screening samples are designated with a Roman numeral "III." Superscript and subscripts are assigned (as for flushing samples above) to reflect sample collection time and source stream. Later nomenclatures were shortened to simply a letter (F,P) to indicate whether the sample was collected from the recirculating feed (F) solution or the permeate (P) stream and a numerical value indicating time elapsed (in hours - hrs) from the beginning of the test phase to the time of sampling.

1. Spike the 9 (or 7*) gallons of inorganic matrix water from the blank determination above with the organic concentrates prepared following the SOP in Appendix D. Mix the spiked water for 0.5 hour to assure good dissolution.

2. Restart the RO system and sample the feed stream at 0.08 hour (5 minutes). Run the system on total recycle with permeate and reject streams to the reservoir.

3. Sample feed and permeate streams at 4.0 hours to determine solute retention, membrane rejection, and solute loss due to adsorption and volatilization.

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APPENDIX B

STANDARD OPERATING PROCEDURE FOR DONNAN MEMBRANE/ORGANIC SOLUTE RETENTION SCREENING

A. Flush Procedure

Flushing of the system is accomplished by completing the following four operations. If samples are collected during the flush sequence, they will be designated with a Roman numeral "I" and assigned a subscript to designate the time (in hours) the sample is collected in the sequence and a letter superscript to designate whether the sample is from the feed (F) or salt strip solution (S). Later nomenclatures were shortened to simply a letter (F,S) to indicate whether the sample was collected from the recirculating feed solution(F) or the salt strip solution (S) and a numerical value indicating time elapsed (in hours - hrs) from the beginning of the test phase to the time of sampling.

1. Establish concentrate and salt strip solution flow loops by proper valve selection.

2. Flush the Donnan system with 2 changes of organic free water (2 hours each).

   a. Each change should be 20 gallons of OFW. Run the first 1 gallon to waste, then recycle the remaining 19.
   b. Each salt strip solution should be 12 liters of 1M NaCl in OFW. Run the first 3 liters to waste, then recycle the remaining 9 liters.
   c. Startup - Initiate flow through the concentrate loop and then through the salt strip loop.
   d. Shutdown - Terminate flow first in the salt strip loop. Wait 5 minutes. Terminate flow in the concentrate loop.
   e. Drain - The concentrate loop using the reverse osmosis drain mode and Donnan drain mode. Shut off the main RO valve when not draining.

3. Continue to flush the Donnan system with 2 changes of 5X inorganic matrix water (1 hour each).

   a. Each change should be 9 gallons each of 5X inorganic matrix water.
   b. Each salt strip solution should be 9 liters of 1M NaCl in OFW.

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c. Startup - Initiate flow through the concentrate loop and then through the salt strip loop.

d. Shutdown - Terminate flow first in the salt strip loop. Wait 5 minutes. Terminate flow in the concentrate loop.

e. Drain - The concentrate loop using the reverse osmosis drain mode and Donnan drain mode. Shut off the main RO valve when not draining.

4. Finish flush procedure by single pass flush with 9 gallons 5X inorganic matrix water on concentrate side and 9 liters of OFW on salt strip side.

B. System Blank

The system blank is determined by analyzing an inorganic matrix water sample before and after an extended period of recirculation in contact with the membrane system. Blank samples are designated with a Roman numeral "II." Superscript and subscripts are assigned (as for flushing samples above) to reflect sample collection time and source stream. Later nomenclatures were shortened to simply a letter (F,S) to indicate whether the sample was collected from the recirculating feed soluton (F) or the salt strip solution (S) and a numerical value indicating time elapsed (in hours - hrs) from the beginning of the test phase to the time of sampling.

1. Recirculate a 7 gallon batch of 5X inorganic matrix water (with stirring) against 9 liters of OFW in the salt strip loop. Samples at 0.08 hour (5 minutes).

2. Continue to recirculate the 7 gallon batch for another 3 hours and resample the concentrate feed. Turn the Donnan system off.

C. Membrane Solute Screening

The retention of specific organic compounds by the Donnan membranes is determined by measuring the concentration of selected compounds in both feed and salt solution streams after a period of operation to allow the system to equilibrate. The following steps are designed to accomplish this objective. Solute screening samples are designated with a Roman numeral "III." Superscript and subscripts are assigned (as for flushing samples above) to reflect sample collection time and source stream. Later nomenclatures were shortened to simply a letter (F,S) to indicate whether the sample was collected from the recirculating feed solution (F) or the salt strip solution (S) and a numerical value indicating time elapsed (in hours - hrs) from the beginning of the test phase to the time of sampling.

1. Spike the 7 gallons of inorganic matrix water from the blank determination above with the organic concentrates prepared following the SOP in Appendix D. Mix the spiked water for 0.5 hour to assure good dissolution.

2. Restart the Donnan system (following start-up procedure in step A.2.c) and sample the feed stream at 0.08 hour (5 minutes). Recirculate 1M NaCl (9 liters) on the salt strip side of the membrane.

3. Sample feed and salt solution streams at 4.0 hours to determine solute retentions and solute losses due to adsorption and volatilization. Maintain temperatures at 20°C. Note volume changes during the screening run.

4. Shut down the system according to A.2.d, above.

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APPENDIX C

STANDARD OPERATING PROCEDURE FOR PREPARATION OF INORGANIC MATRIX WATER

A. **Supplies**

1. H_2O - organic free water
2. HCl - reagent grade
3. NaOH - reagent grade
4. $NaHCO_3$ - anhydrous reagent grade
5. $CaCl_2 \cdot 2H_2O$ - reagent grade
6. $CaSO_4$ - anhydrous reagent grade

B. **Procedure**

1. The following weights of chemicals should be added to each gallon of organic free water to provide a 1X salt mixture ($NaHCO_3$ 70 mg/l; $CaSO_4$ 120 mg/l; $CaCl_2 \cdot 2H_2O$ 47 mg/l).

    a. 0.267 g $NaHCO_3$
    b. 0.178 g $CaCl_2 \cdot 2H_2O$
    c. 0.453 g $CaSO_4$

2. The sequence of addition of chemicals is as follows:

    a. dissolve $NaHCO_3$
    b. adjust pH to pH 5
    c. dissolve $CaCl_2 \cdot 2H_2O$
    d. dissolve $CaSO_4$

3. To obtain quantities other than 1.0 gallon and/or concentrations other than 1X multiply the amount of additives by the new concentration factor and/or new volume (in gallons).

APPENDIX D

STANDARD OPERATING PROCEDURE FOR PREPARATION OF SPIKED WATER FOR MEMBRANE SCREENING RUNS

A. Preparation of Batch of Inorganc Matrix Water

Prepare a batch of inorganic matrix water consisting of 208 liters (55 gallons) at a 5X mixed salt level. Follow the protocol detailed in Appendix C.

B. Preparation of the Acetone Soluble Fraction of Model Organic Compounds

1. Preparation of the acetone concentrate - add the following compounds to a 500 ml volumetric flask and dilute to volume with acetone.

    a. 250 mg of isophorone; 2,4-dichlorophenol; biphenyl; quinoline; 2,6-di-tert-butyl-4-methylphenol; caffeine; stearic acid; anthraquinone; bis(2-ethylhexyl)phthalate; trimesic acid; and furfural.
    b. 25 mg of 1-chlorododecane and 2,2',5,5'-tetrachlorobiphenyl
    c. 190 μl chloroform
    d. 353 μl methylisobutyl ketone
    e. 2,4-dichlorobiphenyl (only on run so designated)

2. Preparation of final level aqueous/organic spiked water - see E.1, below.

C. Preparation of the Water Soluble Fraction of Model Organic Compounds

1. Preparation of initial aqueous concentrate.

    a. Secure two 3.78 liter (1.0 gallon) portions of the 5X inorganic matrix water prepared in step A.
    b. Add the following compounds to one of the 3.78 liter (1.0 gallon) portions of 5X inorganic matrix water.

        1) 85 mg glycine
        2) 42 mg 5-chlorouracil

c. Add the following compound to the other 3.78 liter (1.0 gallon) portion of inorganic matrix water.
42 mg 5-chlorouracil

d. Stir each until dissolved.

2. Preparation of final level aqueous/organic spike water - see E.2, below.

D. Preparation of the Humic Acid Fraction

1. Preparation of initial aqueous concentrate.

a. Collect 1.0 liter of organic free water and adjust to pH 10 with sodium hydroxide.
b. Dissolve 80 mg of humic acid into the liter of pH adjusted water.
c. Adjust the liter of humic acid concentrate to 5X inorganic salts following protocol in Appendix C.
d. Filter the solution using a prerinsed Buchner and glass fiber filter assembly.

2. Preparation of the final level aqueous/organic spike water - see E.3, below.

E. Blending of the Various Organic Fractions to Prepare the Test Challenge Water

1. Addition of the acetone soluble fraction - pump 167 ml of the acetone concentrate prepared in step B.1 into inorganic matrix water. Rinse pump and line with two 15 ml portions of acetone.

2. Addition of the water soluble fractions - pour the two 3.78 liter (1.0 gallon) portions of water soluble compounds into the 5X inorganic matrix water. Minimize exposure to the air.

3. Addition of humic acid fraction - pour the 1.0 liter of humic acid concentrate into the 5X inorganic matrix water.

4. Blending - stir the solution for 0.5 hour to homogenize the solution. Minimize exposure to the air.

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APPENDIX E

STANDARD OPERATING PROCEDURE FOR PREPARATION OF SPIKED WATER FOR MEMBRANE CONCENTRATION RUNS

A. Preparation of Batch of Inorganic Matrix Water

Prepare a batch of inorganic matrix water consisting of 44 (43 in test using humic acid) gallons of 1X inorganic salts. Follow the protocol outlined in Appendix C.

B. Dosing with Acetone Soluble Fraction of Model Organic Compounds

1. Preparation of acetone concentrate add the following compounds to a 500 ml volumetric flask and dilute to volume with acetone.

   a. 74.5 mg of isophorone; 2,4-dichlorophenol; biphenyl; quinoline; 2,6-di-tert-butyl-4-methyl phenol; caffeine; stearic acid; anthraquinone; bis(2-ethylhexyl)phthalate; trimesic acid; and furfural.
   b. 7.5 mg of 1-chlorododecane, and 2,2',5,5'-tetrachlorobiphenyl.
   c. 50 µl chloroform.
   d. 93 µl methylisobutyl ketone.
   e. 2,4-dichlorobiphenyl (only on the runs so designated).

2. Preparation of an intermediate level aqueous/organic concentrate.

   a. Temporarily remove 3 gallons of 1X inorganic matrix water from the 44 (or 43) gallons prepared in part A.
   b. Add 56.0 ml of the acetone concentrate prepared previously (B.1), stir briefly, and examine for solute dissolution. Minimize aeration.

3. Preparation of the final level aqueous/organic spike water. Add the 3.0 gallon intermediate level concentrate back into the remaining 40 (39) gallons of inorganic matrix water as directed in E.1, below.

C. Dosing with Water Soluble Fraction of Model Organic Compounds

1. Preparation of initial aqueous concentrate.

   a. Temporarily remove 1.0 gallon of 1X inorganic matrix water

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from the 44 (or 43) gallons prepared in step A.

b. Add the following compounds to the 1.0 gallon of 1X inorganic matrix water.

1) 8.4 mg of 5-chlorouracil.
2) 8.4 mg of glycine.
3) 3.3 mg of lead nitrate $[Pb(NO_3)_2]$.[*]
4) 8.4 mg glucose

2. Preparation of final level aqueous/organic spike water. Add the 1.0 gallon of concentrate prepared in step C.1, above, back into the remaining 43 (or 42) gallons of inorganic matrix water as directed in E.2, below.

D. Dosing With Humic Acid[†]

1. Preparation of initial aqueous concentrate.
    - a. Collect 1.0 gallon of organic free water and adjust to pH10 using NaOH.
    - b. Dissolve 334 mg of humic acid into the gallon of pH adjusted water.
    - c. Adjust the gallon of humic acid concentrate to 1X inorganic salts following protocol in Appendix C.
    - d. Filter the solution after stirring overnight. Use a prerinsed Buchner and glass fiber filter assembly.

2. Preparation of final level aqueous/organic spike water - see E.3, below.

E. Blending Of Various Organic Fractions To Prepare The Test Challenge Water

1. Addition of the acetone soluble fraction. Pour the 3.0 gallons of intermediate level concentrate into the 40 (or 39) gallons of inorganic matrix water while minimizing exposure to the air.

2. Addition of the water soluble fraction. Pour the 1.0 gallon of concentrate prepared in C.1, above, into the 43 (or 42) gallons of inorganic matrix water while minimizing exposure to the air.

3. Addition of the humic acid fraction. Pour the 1.0 gallon of humic acid concentrate into 43.0 gallons of inorganic matrix water while minimizing exposure to the air.[**]

4. Blending - Stir briefly to homogenize the solution. Minimize exposure to the air.

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[*] These compounds are to be used only in runs so designated.
[†] This procedure only applies to runs requiring humic spike.
[**] This procedure only applies to runs requiring humic spike.

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APPENDIX F

STANDARD OPERATING PROCEDURE FOR REVERSE OSMOSIS - DONNAN SOFTENING/ORGANIC SOLUTE CONCENTRATION TEST

A. Flush Procedure

1. Flush the Donnan softening subsystem. Follow step A of the Donnan membrane/organic solute retention screening protocol (Appendix B) using a 1X rather than 5X inorganic salt matrix water.

2. Flush the reverse osmosis concentration subsystem. Follow step A of the reverse osmosis membrane/organic solute retention screening protocol (Appendix A) using 1X rather than 5X inorganic salt matrix water.

B. System Blank

No system blank determinations will be repeated for the concentration runs.

C. Membrane-Solute Concentration

1. Prepare the spike water according to Appendix E.

2. Perform the first stage reverse osmosis concentration following the guidelines below.

   a. Drain the system of as much water as possible without complete disassembly.
   b. Transfer 44 gallons of challenge water to the process drum - SAMPLE DURING THE TRANSFER.
   c. Start the reverse osmosis system with permeate routed to calibrated 15 gallon carboys. Establish and maintain the following operating conditions:

      1) 400 psig pressure
      2) pH control 4.5 - 5.5
      3) temperature 20 ± 1°C
      4) rejection > 93 percent (inorganic salts at 1X)

   d. Monitor salt rejection at approximately the following concentrations. Minimize sample volume and return uncontaminated sample to the system.

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    1) ∼1X volumetric concentration
    2) ∼10X volumetric concentration

  e. Collect a feed and permeate pair of samples at ∼8X concentration level for analysis of organic compounds.
  f. Terminate the first stage reverse osmosis concentration when the volume remaining is 3.5 gallons (∼12.6X). Drain the system into a clean vessel, seal, and store at 4°C until needed.
  g. Repeat steps a-d and f for each of the remaining two batches of challenge water.

3. Donnan Dialysis Softening - Follow the guidelines below.

  a. Return the three batch concentrates prepared above to the process reservoir and stir with propeller stirrer (∼5 minutes).
  b. Initiate flow in the Nafion units (feed/concentrate side) as detailed in Appendix B. Collect a sample of feed within 5 minutes of initiation of flow. Next, initiate flow through the salt strip loop.
  c. Continue to run the Nafion softening unit for 4 hr. Run the reverse osmosis loop (with permeate on recycle) for 2 minutes each 30 minutes to advance this holdup volume into the process drum.
  d. Sample both the feed and the salt strip solution at the end of the 4-hr softening period. Sample prior to shutdown of the process. Terminate softening as detailed in Appendix B.

4. Perform the final stage reverse osmosis concentration following the guidelines below.

  a. Switch the valving to route permeate to a calibrated carboy. This will be used for estimation of the volume of water processed.
  b. Start the reverse osmosis system. Maintain normal process conditions.
  c. Monitor the salt rejection at the following concentrations.

    1) ∼20X volumetric concentration
    2) ∼30X volumetric concentration

  d. Collect a feed and permeate pair of samples at ∼40X concentration level for analysis of organic compounds.
  e. Terminate the run at 50X concentration. Drain the system into a 5 gallon jug and measure the volume. Draw samples of the concentrate for analysis of organic compounds.

5. Flush both systems with two 20 gallon batches of OFW.

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APPENDIX G

STANDARD OPERATING PROCEDURE FOR GROUP 1: SEMIVOLATILE EXTRACTABLE COMPOUNDS

A. Scope and Application

This method is applicable to the determination of the 13 Group 1 semivolatile extractable compounds in an aqueous matrix over the concentration range listed below.

1)	methyl isobutyl ketone	50 ng/ml - 2500 ng/ml
2)	isophorone	50 ng/ml - 2500 ng/ml
3)	2,4-dichlorophenol	50 ng/ml - 2500 ng/ml
4)	quinoline	5 ng/ml - 2500 ng/ml
5)	biphenyl	5 ng/ml - 2500 ng/ml
6)	1-chlorododecane	5 ng/ml - 2500 ng/ml
7)	2,6-di-tert-butyl-4-methylphenol	50 ng/ml - 2500 ng/ml
8)	2,4'-dichlorobiphenyl	5 ng/ml - 2500 ng/ml
9)	caffeine	50 ng/ml - 2500 ng/ml
10)	2,2',5,5'-tetrachlorobiphenyl	5 ng/ml - 2500 ng/ml
11)	anthraquinone	5 ng/ml - 2500 ng/ml
12)	stearic acid	50 ng/ml - 2500 ng/ml
13)	bis(2-ethylhexyl)phthalate	50 ng/ml - 2500 ng/ml

B. Summary of Method

Batch liquid-liquid extraction is used to extract and concentrate Group 1 compounds from aqueous samples. This method is a modified version of method 625 (Federal Register, Monday, December 3, 1979.) Four surrogate standards are used: 2-heptanone, 2,4,6-trichlorophenol, 2,3,5,6-tetrachlorophenol, and d_{10}-anthracene. At pH 11, 7, and 2 the aqueous sample is extracted with three serial aliquots of methylene chloride. The organic extracts are combined and dried with sodium sulfate. The dried extract is evaporated to a volume of 4 ml by using Kuderna-Danish evaporation techniques and further concentrated to 0.5-1 ml by nitrogen blowdown using a micro-Synder column. The concentrated extract is analyzed by capillary column gas chromatography. An internal standard method is used for quantification; 1-fluoronaphthalene is the internal standard.

C. Apparatus and Materials

1. Separatory funnel with Teflon stopcock. 250 ml volume for 100 ml

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sample size, 2 liter volume for 1 liter sample size.

2. Drying column. Pack 150 ml capacity cylindrical funnel with pre-cleaned glass wool plug and 2 inches of cleaned and dried sodium sulfate (muffled at 400°C to remove organic materials).

3. Kuderna-Danish (K-D) apparatus.

   a. Three-ball macro-Synder column, size 121 (Kontes #K-503000-0121).
   b. Evaporative flask (Kontes #K-57001-0500). 500 ml capacity with 24/40 top joint and 19/22 lower joint.
   c. Concentrator tube (Kontes #K-570050-0425). Graduated 4 ml capacity with 19/22 joint.
   d. Micro-Snyder column, 19/22 joint (Kontes #K-569251-0319).
   e. Springs 0.5 inch to attach 3c to 3b (Kontes #K-662750-0012).

4. Glass boiling beads.

5. Heated water bath with concentric ring cover capable of temperature control. Locate bath in a hood.

6. UHP nitrogen.

7. Capillary column gas chromatograph/flame ionization detection system capable of temperature programming and splitless mode injection. Column - J&W fused silica capillary column, SE 54 liquid phase, 30 m x 0.251 mm.

D. Reagents

1. Sodium hydroxide (ACS grade), 6N in distilled water.

2. Sulfuric acid (ACS grade), 6N in distilled water.

3. Sodium sulfate, reagent grade anhydrous powder. Preclean by rinsing twice in nanograde methylene chloride then oven dry at 110°C.

4. Methylene chloride, nanograde or equivalent.

5. Acetone, nanograde or equivalent.

6. QA/QC standards

   a. Surrogate standards:*
      2-heptanone (98+% purity Eastman Organic Chemicals)
      2,4,6-trichlorophenol (95+% purity Supelco)

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*Note: All surrogates are available from Aldrich at 98+% purity.

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2,3,5,6-tetrachlorophenol (95+% purity Supelco)
d_{10}-anthracene (98 + atom % D Merck, Sharp, and Dohm Isotopes, Montreal, Canada)

b. Internal standard:
1-fluoronaphthalene (98% purity Aldrich)

E. Procedure

1. The technique is described below for a 1000 ml sample volume. Adjust the procedural details according to sample volume. For sample volumes approximating 100 ml, use 10 ml aliquots of methylene chloride for the serial extractions. With each extraction set on a given day, a distilled water method blank is processed exactly as the samples.

2. Place a 1 liter aliquot of sample into a 2 liter separatory funnel. Spike the sample with 500 µl of a stock surrogate standard prepared in nanograde acetone. (Surrogate stock contains 250 ppm each of 2-heptanone, 2,4,6-trichlorophenol, 2,3,5,6-tetrachlorophenol and d_{10}-anthracene.) Adjust sample to pH 11 with 6N NaOH. Multi-range pH paper is used for the measurement.

3. Add 60 ml of methylene chloride to separatory funnel. Shake for 2 minutes, carefully venting funnel at periodic intervals. Let stand for 10 minutes to allow complete separation of the two phases. Collect the methylene chloride extracts into a 1 liter Erlenmeyer flask.

4. Repeat Step 3 two more times, combining the extracts in the Erlenmeyer flask.

5. Adjust the previously pH 11 extracted aqueous sample to pH 7 with 6N H_2SO_4. Serially extract with three 60 ml aliquots of methylene chloride. Collect and combine all the extracts in the same Erlenmeyer flask used in Step 4.

6. Adjust the previously pH 11 and pH 7 extracted aqueous sample to pH 2 with 6N H_2SO_4. Serially extract with three 60 ml aliquots of methylene chloride. Collect and combine all the extracts in the same Erlenmeyer flask used in Steps 4 and 5.

7. Remove water from the methylene chloride extract by adding excess cleaned and dried sodium sulfate. Agitate mixture. Pour the semi-dried extract through the sodium sulfate drying column. Rinse the bulk sodium sulfate drying vessel (Erlenmeyer flask from Step 6) and drying column with three additional 5 ml portions of solvent and add rinsings to extract.

8. Collect the extract and rinsings from Step 7 in a 500 ml K-D flask equipped with a 4 ml concentrator tube containing a glass boiling bead. Pre-calibrate the concentrator tube remembering to compensate for the volume of the boiling bead. Attach the three-ball macro-Snyder column. Place the K-D apparatus on a warm water bath with the concentrator tube partially immersed in the water. Optimize the vertical position of the apparatus and

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the water temperature for the solvent and apparatus. When the liquid has reached an apparent volume of less than 4 ml remove the K-D apparatus from the heat and allow to cool. Remove the Snyder column. With 1 to 2 ml of solvent, rinse the evaporative flask and its lower joint into the concentrator tube.

9. To the 4 ml concentrator tube in Step 8, attach the micro-Snyder column. Connect a transfer pipette by Teflon tubing to an UHP nitrogen gas tank. Place the transfer pipette in the micro-Snyder column above the solvent level. Gently blow a stream of nitrogen over the solvent surface until the volume is reduced to approximately 1 ml. Rinse the sides of the concentrator tube with approximately 0.5 ml of solvent. Reduce volume of extract to 0.5 or 1.0 ml. Spike with internal standard. (For 1 ml extract spike with 10 μl of a 10,000 ppm 1-fluoronaphthalene secondary standard in nanograde methylene chloride; prepare by 1:10 dilution of a stock 100,000 ppm 1-fluoronaphthalene standard in nanograde acetone.) Record exact final volume.

F. Analysis

1. Analyze the sample extract by capillary column gas chromatography/flame ionization detection. Data is obtained on HP Model 5710A GC/FID in the splitless mode equipped with HP 7671A automatic sampler and HP-3385A automation system.

2. Instrument conditions are as follows:

Column:	30 m x 0.25 mm J&W fused silica, SE-54 liquid phase
Temperature program:	30°C (8 min) to 300°C at 8°C/min (hold 8 min)
Backflush flow:	60 ml/min (activated 35 sec after injection)
Carrier gas:	1 ml/min UHP He
Column pressure:	20 psi
Air flow:	150 ml/min
H_2 flow:	45 ml/min
Injection port temperature:	250°C
Detector temperature:	300°C
Sample injection volume:	1 μl, splitless mode

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Figure 1-1 shows the separation achieved by the column. The corresponding peak identification is given in Table 1-1.

3. The internal standard method with integrated peak areas is used for quantification. First, response factors (RF) are calculated from standards by equation 1. The internal standard is 1-fluoronaphthalene.

$$\text{Eq(1)} \qquad RF = \frac{A_x\ (\text{std})\ C_{is}\ (\text{std})}{A_{is}\ (\text{std})\ C_x\ (\text{std})}$$

where:

A_x = Integrated area of compound of interest in standard.
C_{is} = Amount (ng) of 1-fluoronaphthalene in standard.
A_{is} = Integrated area of 1-fluoronaphthalene in standard.
C_x = Amount (ng) of compound of interest in standard.

Next, the concentration of the compound of interest (C_o) in ng/ml in the sample is calculated using equation 2.

$$\text{Eq(2)} \qquad C_o\ (\text{ng/ml}) = \frac{A_x\ (\text{spl})\ C_{is}\ (\text{spl})\ \dfrac{V_t}{V_i}}{A_{is}\ (\text{spl})\ RF \qquad V_o}$$

where:

A_x = Integrated area of compound of interest in sample.
C_{is} = Amount (ng) of 1-fluoronaphthalene in sample.
V_t = Volume of total extract (µl).
V_i = Volume of extract injected (µl).
A_{is} = Integrated area of 1-fluoronaphthalene in sample.
RF = Response factor.
V_o = Volume of water extracted (ml).

Finally, the concentration of the compound of interest is corrected for surrogate standard recovery and any compound contamination found in the corresponding method blank. Listed below is each Group 1 compound and its corresponding surrogate standard chosen with consideration to similar chemical behavior.

Compound	Surrogate Standard
methyl isobutyl ketone	2-heptanone

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isophorone	d_{10}-anthracene
2,4-dichlorophenol	2,4,6-trichlorophenol
quinoline	d_{10}-anthracene
biphenyl	d_{10}-anthracene
1-chlorododecane	d_{10}-anthracene
2,6-di-tert-butyl-4-methyl phenol	2,4,6-trichlorophenol
2,4'-dichlorobiphenyl	d_{10}-anthracene
caffeine	d_{10}-anthracene
2,2',5,5'-tetrachlorobiphenyl	d_{10}-anthracene
anthraquinone	d_{10}-anthracene
stearic acid	2,3,5,6-tetrachlorophenol
bis(2-ethylhexyl)phthalate	d_{10}-anthracene

G. Method Evaluation

1. Accuracy and Precision

The analytical protocol was evaluated with separate distilled water samples fortified with the 13 Group 1 compounds at concentrations of about 5.0 ng/ml, 50 ng/ml, 1000 ng/ml, and 2500 ng/ml; samples were prepared in triplicate for each concentration. Results are given in Table 1-2. Method accuracy is represented by the deviation of the mean recovery from 100%; method precision by the standard deviation and coefficient of variation of the triplicate analyses.

2. Linearity

The linearity of the GC/FID response to each of the 13 semivolatile extractable compounds was determined as follows. Standards of the 13 compounds were prepared for at least 7 concentrations ranging from 1 ng/µl to 2500 ng/µl. Each standard was fortified with 100 ng/µl of the internal standard to mimic the levels used to spike actual sample extracts. Figures 1-2 through 1-14 are plots of the linear range for each of the 13 compounds. Linear regression analysis of the points yields the listed slope, y-intercept, and correlation coefficient.

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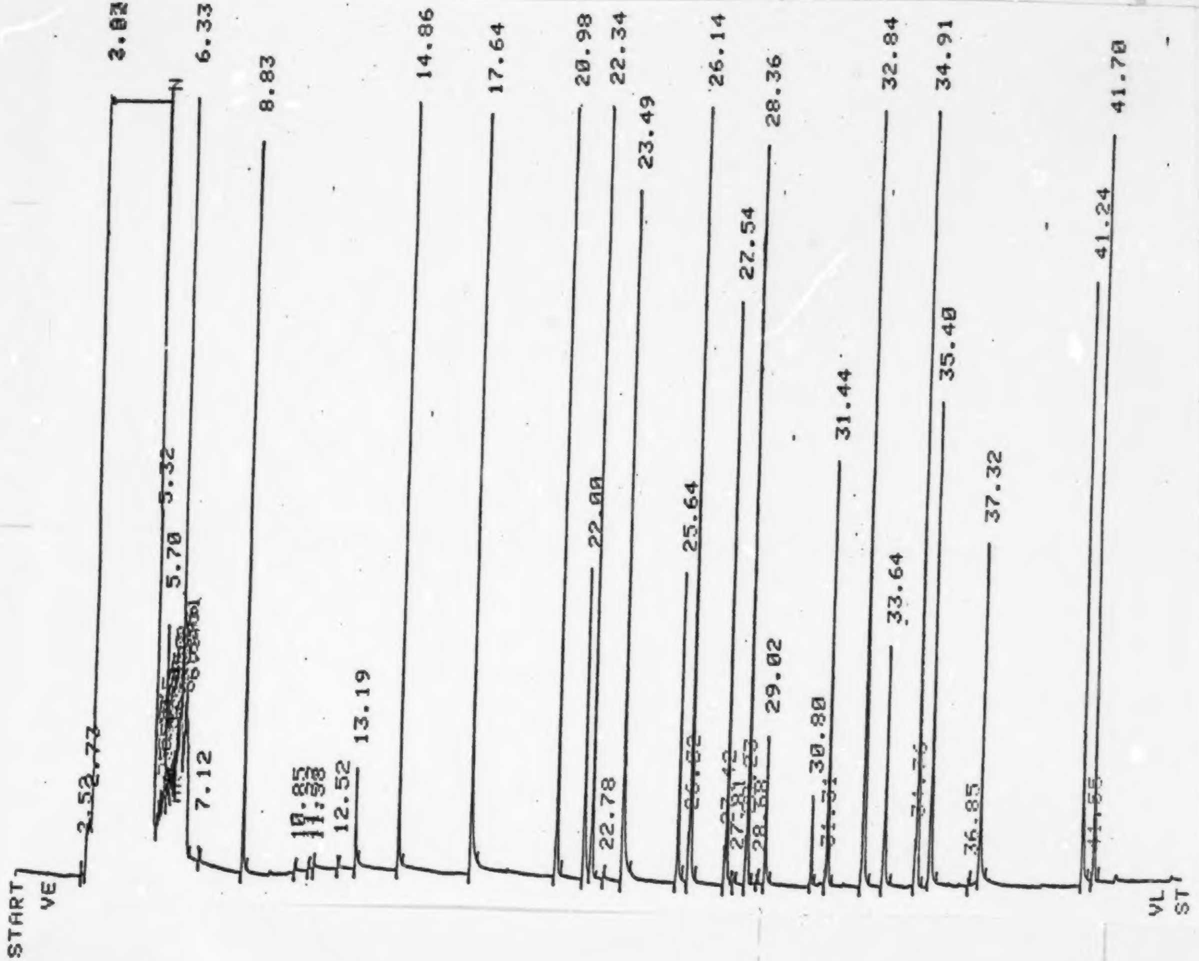

Figure 1-1. GC/FID chromatogram of Group 1 compounds. SE-54 fused silica column, 30°C (8 min) to 300°C/min.

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TABLE 1-1: IDENTIFICATION OF PEAKS IN FIGURE 1-1

Compound	Retention Time
methyl isobutyl ketone	8.83
2-heptanone (SS)	14.86
isophorone	20.98
2,4-dichlorophenol	22.00
1-fluoronaphthalene (IS)	22.34
quinoline	23.49
2,4,6-trichlorophenol (SS)	25.64
biphenyl	26.14
1-chlorododecane	27.54
2,6-di-tert-butyl-4-methylphenol	28.36
2,3,5,6-tetrachlorophenol (SS)	29.02
2,4'-dichlorobiphenyl	31.44
d_{10}-anthracene (SS)	32.84
caffeine	33.64
2,2',5,5' tetrachlorobiphenyl	34.91
anthraquinone	35.40
stearic acid	37.32
bis(2-ethylhexyl)phthalate	41.70

IS = internal standard
SS = surrogate standard

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TABLE 1-2. ACCURACY AND PRECISION OF ANALYTICAL METHOD FOR GROUP 1 ANALYSIS

Compound	Sample Concentration 5 ppb % Recovery mean ± S.D. (CV)	50 ppb % Recovery mean ± S.D. (CV)	1000 ppb % Recovery mean ± S.D. (CV)	2500 ppb % Recovery mean ± S.D. (CV)
methyl isobutyl ketone	--	98 ± 14 (14)	114 ± 5 (4)	92 ± 4 (4)
isophorone	104 ± 13 (13)	105 ± 13 (12)	94 ± 8 (9)	99 ± 8 (8)
2,4-dichlorophenol	NR	95 ± 1 (1)	96 ± 6 (6)	95 ± 14 (15)
quinoline	103 ± 19 (18)	105 ± 13 (12)	107 ± 6 (6)	105 ± 10 (10)
biphenyl	84 ± 34 (40)	93 ± 11 (12)	92 ± 8 (9)	102 ± 10 (10)
1-chlorododecane	133 ± 30 (23)	105 ± 10 (10)	101 ± 10 (10)	108 ± 9 (8)
2,6-di-tert-butyl-4-methylphenol	NR	85 ± 3 (4)	84 ± 9 (11)	92 ± 2 (2)
2,4'-dichlorobiphenyl	101 ± 44 (44)	108 ± 13 (12)	102 ± 6 (6)	117 ± 15 (13)
caffeine	NR	105%, 102%	112 ± 4 (4)	114 ± 5 (4)
2,2',5,5'-tetrachlorobiphenyl	74%, 107%	112 ± 7 (6)	102 ± 4 (4)	122 ± 16 (13)
anthraquinone	120 ± 19 (16)	112%, 103%	103 ± 3 (3)	108 ± 2 (2)
stearic acid	NR	108 ± 1 (1)	--	117 ± 12 (10)
bis(2-ethylhexyl) phthalate	NR	112 ± 8 (7)	95 ± 4 (4)	111 ± 5 (5)

NR = Not Recovered

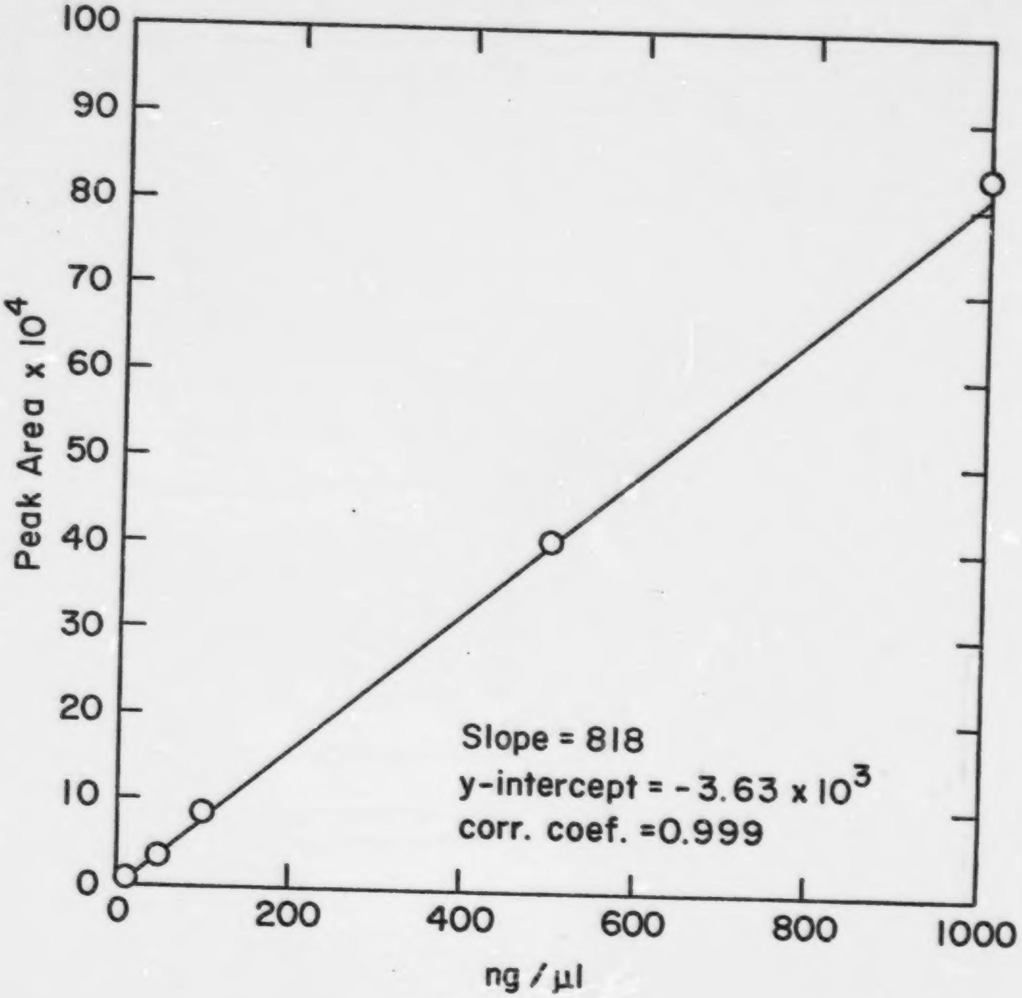

Figure 1-2. Integrated peak area versus MIBK concentration; normalized to area of internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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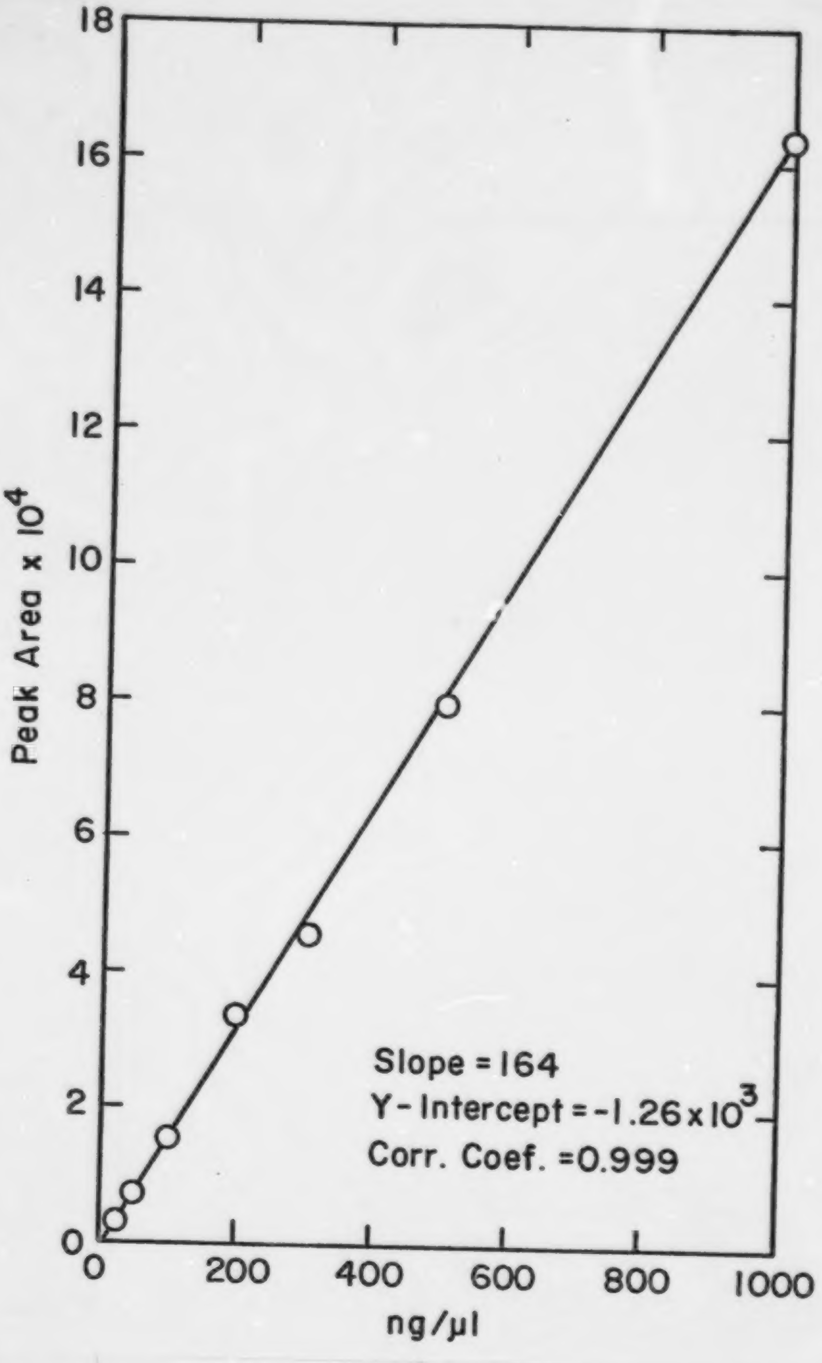

Figure 1-3. Integrated peak area versus isophorone concentration; normalized to area of internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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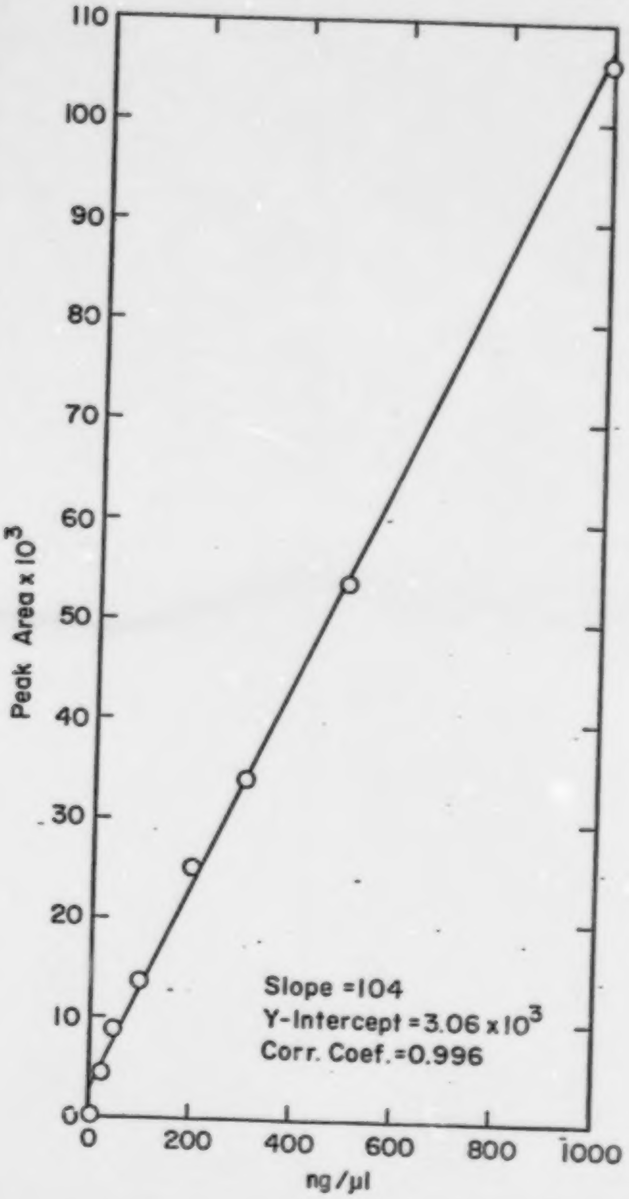

Figure 1-4. Integrated peak area versus 2,4-dichlorophenol concentration; normalized to area of internal standard 1-fluronaphthalene. GC/FID, SE-54 column.

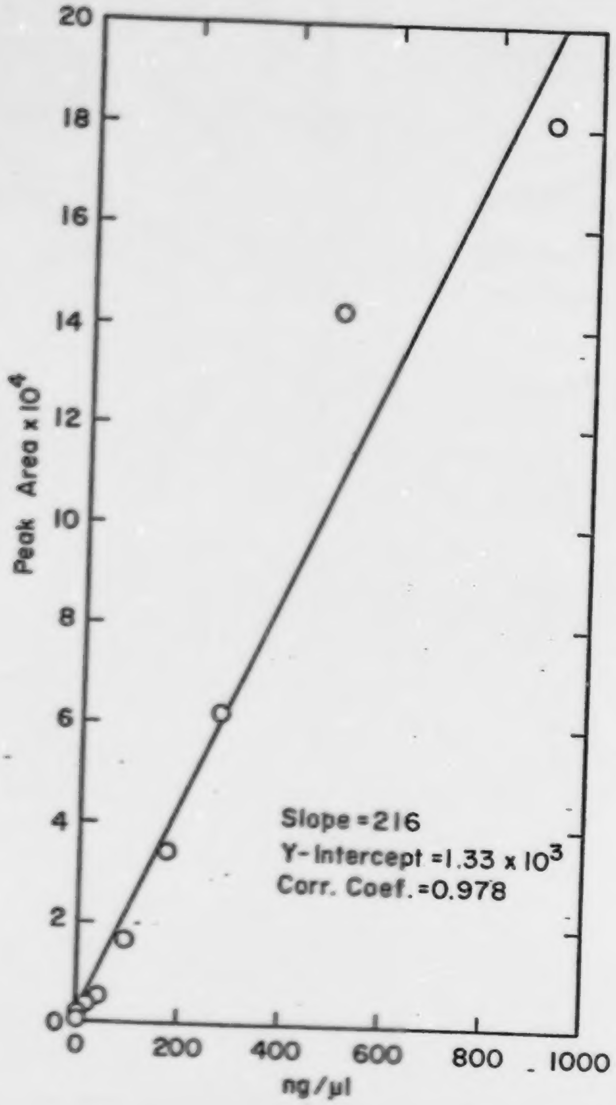

Figure 1-5. Integrated peak area versus quinoline concentration; normalized to internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

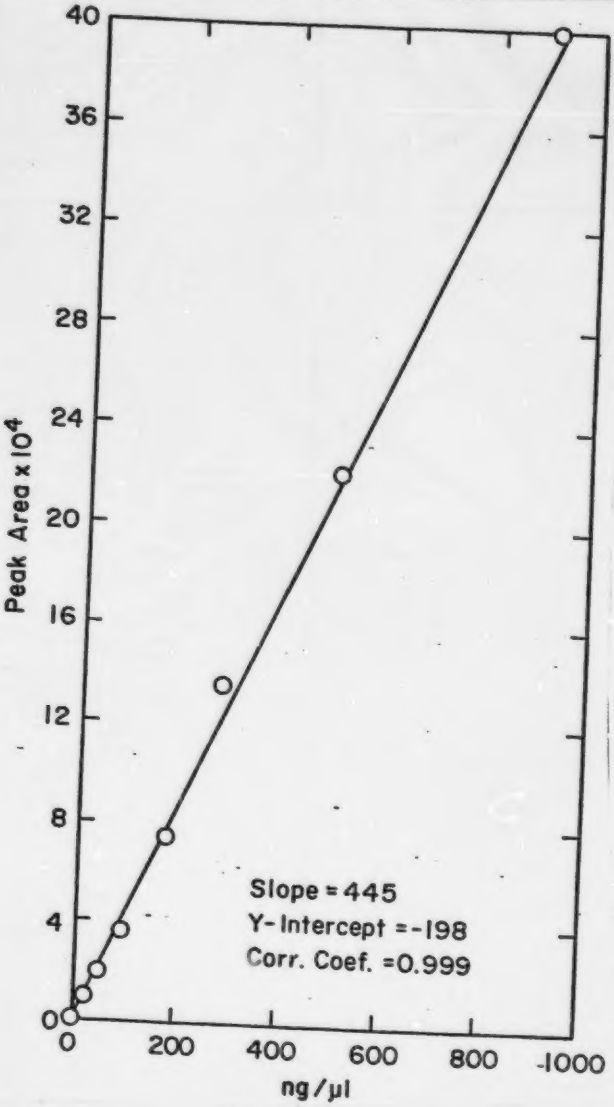

Figure 1-6. Integrated peak area versus biphenyl concentration; normalized to internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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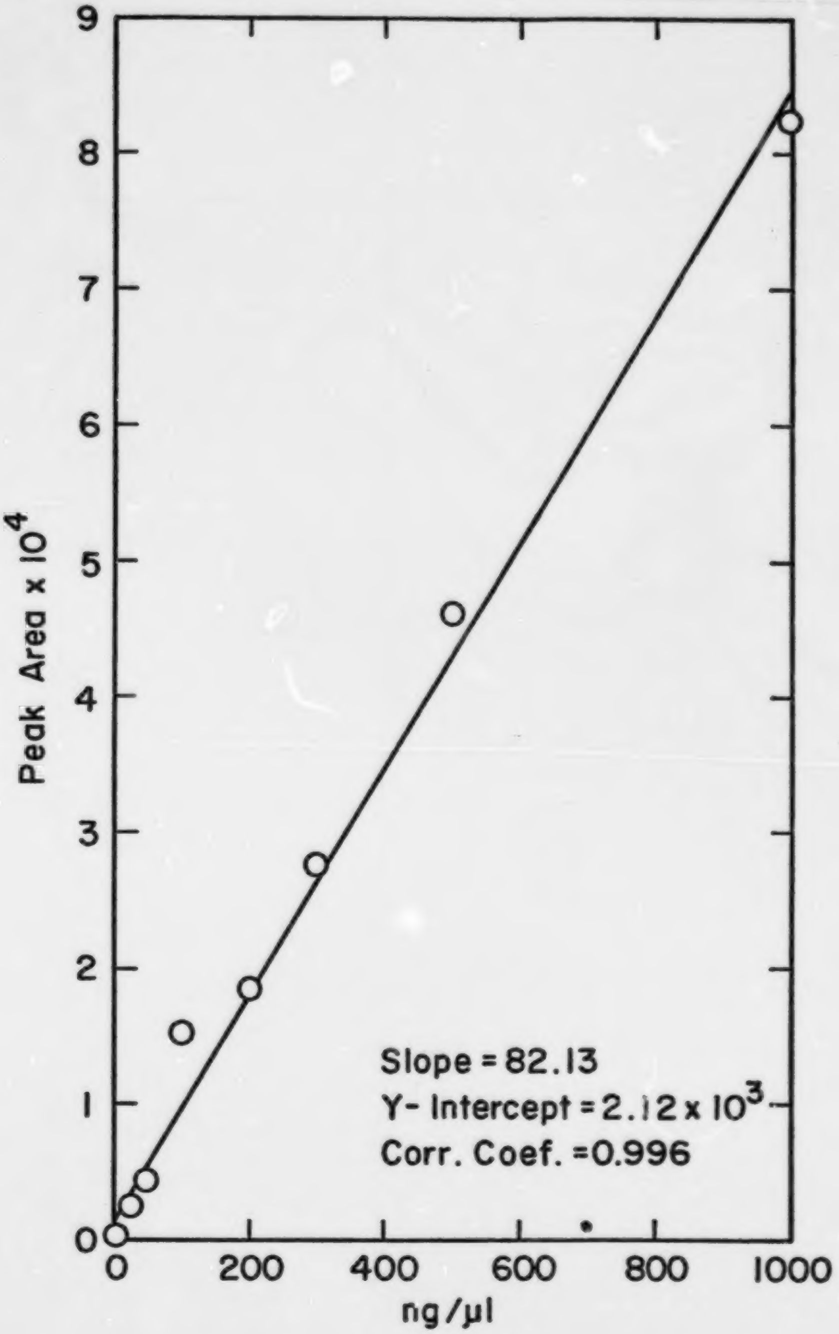

Figure 1-7. Integrated peak area versus 1-chlorododecane concentration; normalized to area of internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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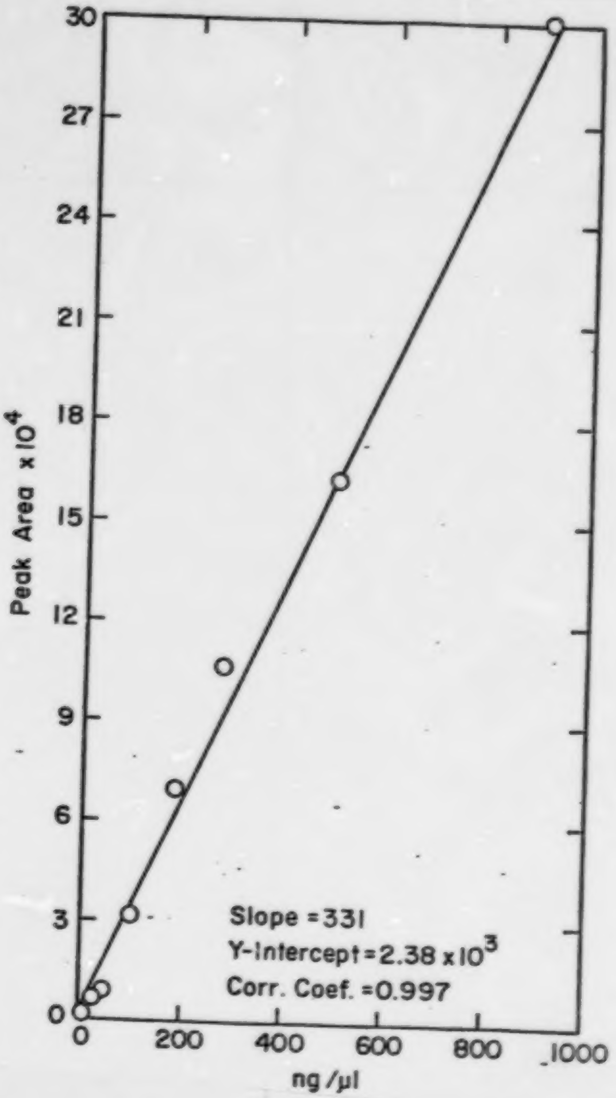

Figure 1-8. Integrated peak area versus 2,6-di-tert-buryl-4-methylphenol; normalized to internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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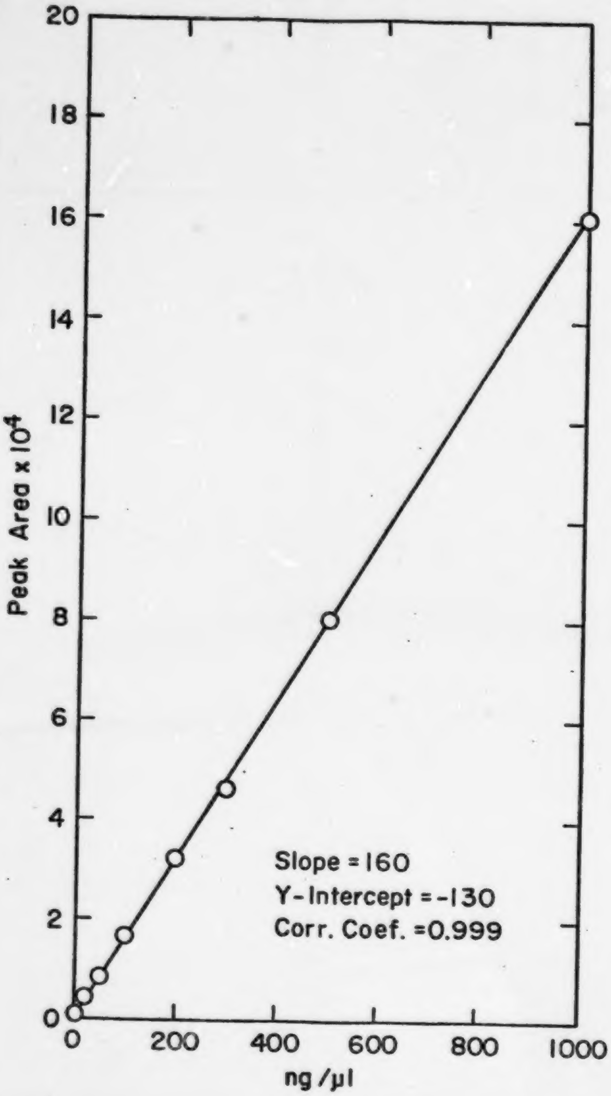

Figure 1-9. Integrated peak area versus 2,4'-dichlorobiphenyl concentration; normalized to area of internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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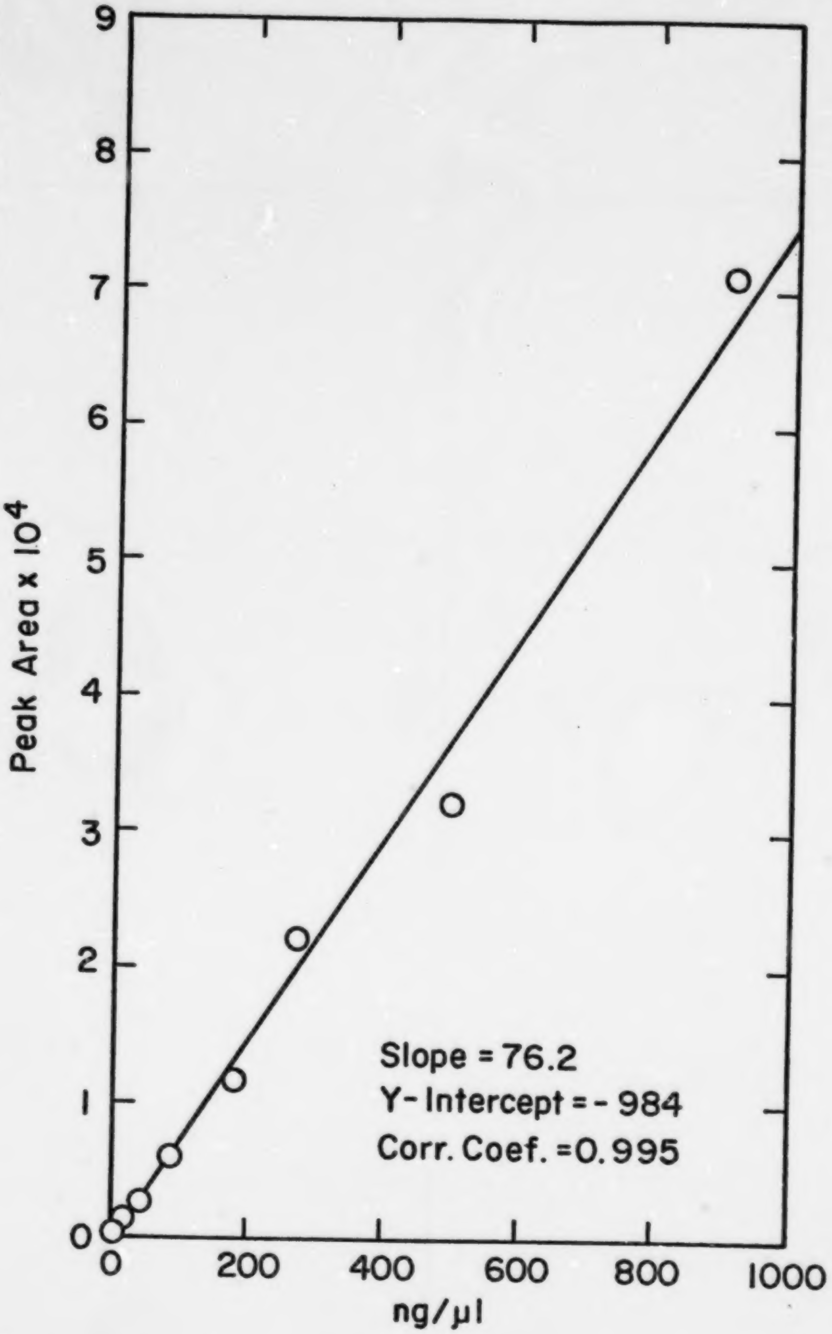

Figure 1-10. Integrated peak area versus caffeine concentration; normalized to area of internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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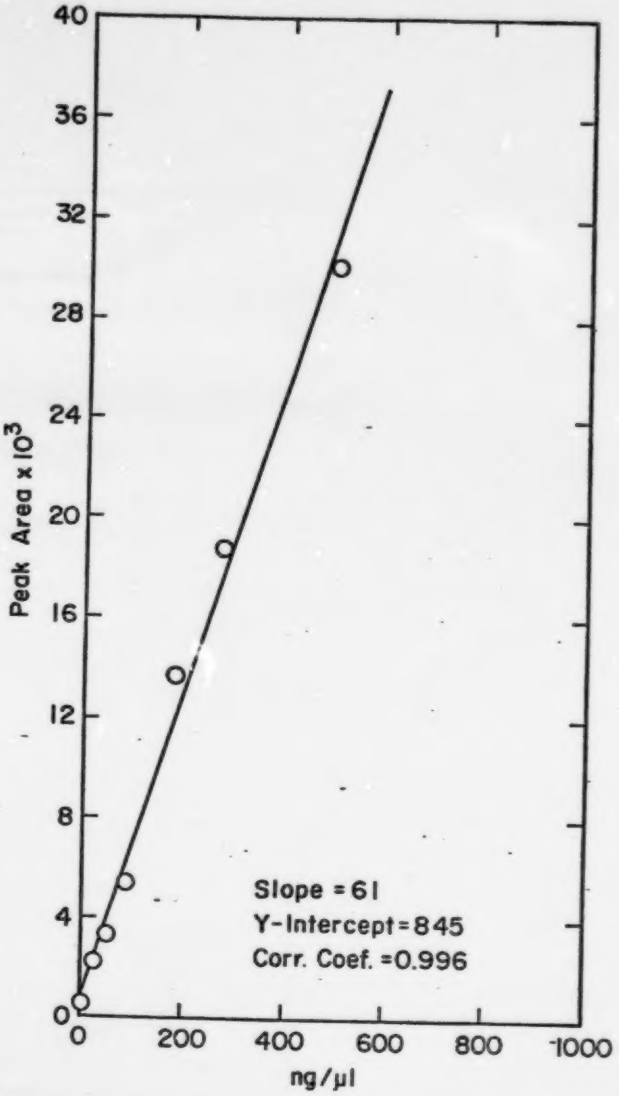

Figure 1-11. Integrated peak area versus 2,2',5,5'-tetrachlorobiphenyl concentration; normalized to area of internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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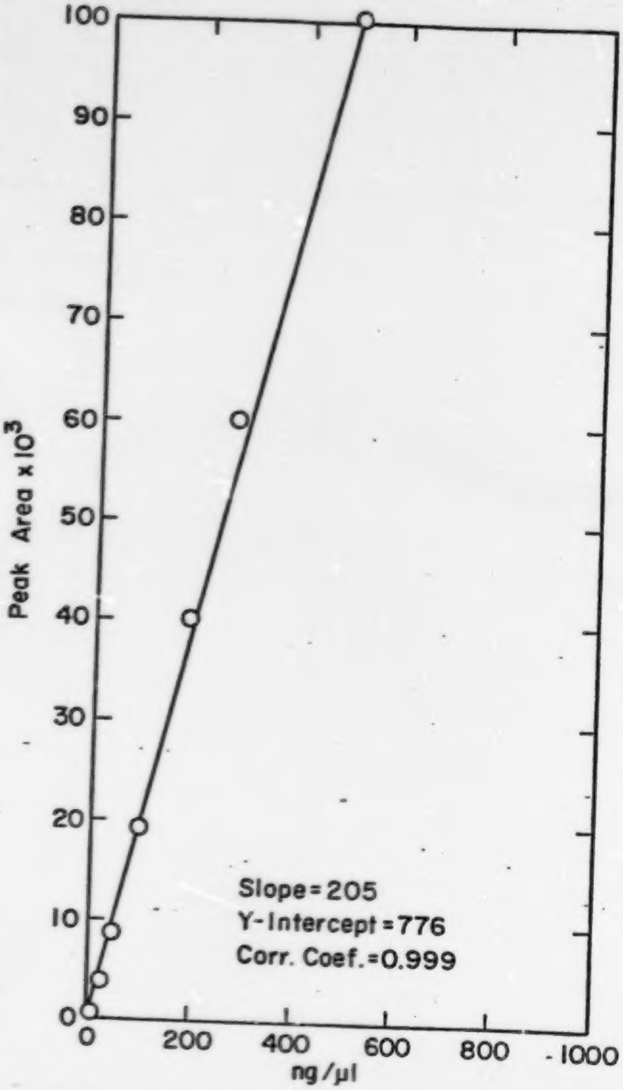

Figure 1-12. Integrated peak area versus anthraquinone concentration; normalized to area of internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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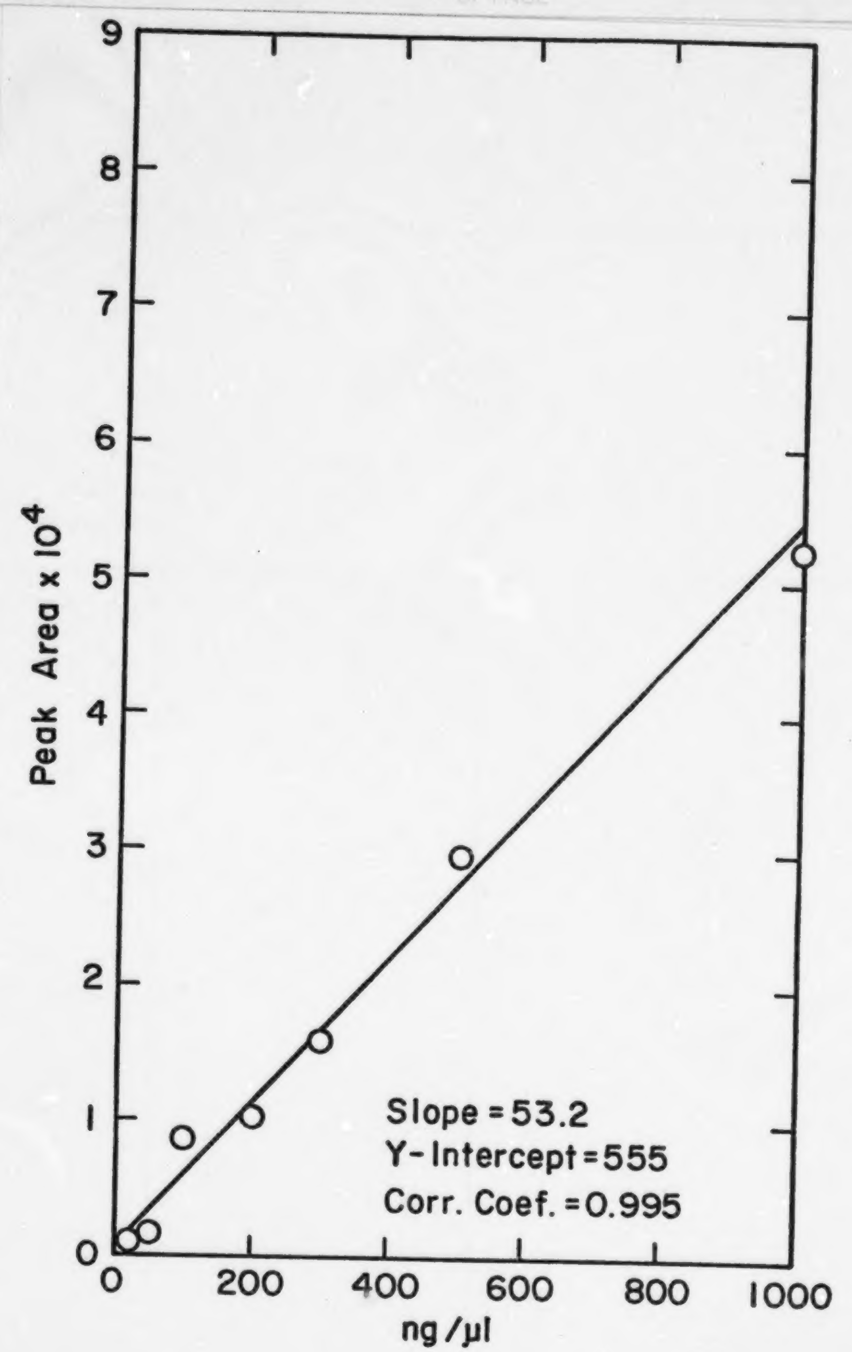

Figure 1-13. Integrated peak area versus stearic acid concentration; normalized to area of internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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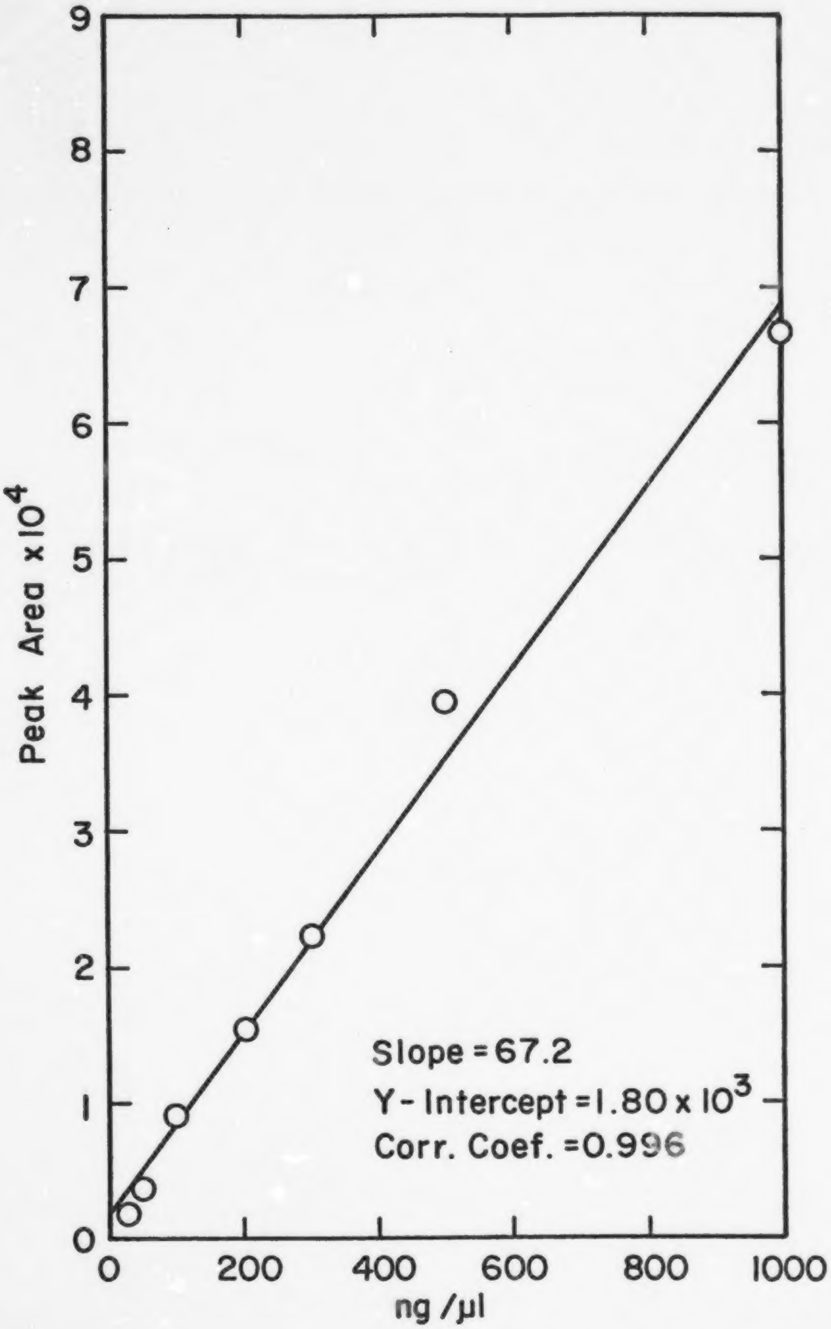

Figure 1-14. Integrated peak area versus bis(2-ethylhexyl)phthalate concentration; normalized to area of internal standard 1-fluoronaphthalene. GC/FID, SE-54 column.

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APPENDIX H

STANDARD OPERATING PROCEDURE FOR
GROUP 2: CHLOROFORM

A. Scope and Application

This method is applicable to the determination of chloroform in an aqueous matrix over the concentration range 50 ng/ml to 2500 ng/ml. There is no interference from the other 21 compounds of interest to this study.

B. Summary of Method

The method used is a slightly modified version of the EPA method (September 9, 1977) entitled "The Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction." An aliquot of the sample is extracted with 1 ml of methylcyclohexane and analyzed by GC with an electron capture detector. The column is 10% Squalane on Chromosorb WAW. The GC is operated isothermally at 67°C. Quantification is based on calibration by external standards.

C. Apparatus and Materials

1. Extraction vessels - 10 ml test tubes with Teflon lined screw caps.

2. Automatic rotary shaker (Scientific Industries, Inc., Model 151).

3. Gas chromatograph with electron capture detector (HP 5830A) with a means for automatic peak integration (HP 18850A). System is equipped with an automatic sampler (HP 7671A).

4. Column - 4 mm ID x 2 mm long glass packed with 10% Squalane on Chromosorb WAW (80/100 mesh).

D. Reagents

1. Methycyclohexane, must be glass distilled prior to use.

2. Acetone, nanograde or equivalent.

3. Chloroform, 99% purity Aldrich.

E. Procedure

1. Pipette 1.0 ml of methylcyclohexane into extraction tube.

2. Pipette either 1 ml or 5 ml of sample into extraction tube (5 ml for 50 to 250 ppb sample range; 1 ml for 250 to 2500 ppb range).

3. Cap the tube; shake for 5 minutes on automatic rotary shaker.

4. Allow the phases to separate (~1 min).

5. Transfer organic layer to GC vial and analyze by GC/EC equipped with automatic sampler.

6. Instrument conditions are as follows:

Instrument:	HP 5830A GC/EC system equipped with HP 7671A automatic sampler and interfaced to HP 18850A terminal
Column:	4 mm ID x 2 mm long, glass, packed with 10% Squalane on Chromosorb WAW (80/100 mesh)
Carrier flow:	20 ml/min 95% Ar/5% methane
Column temperature:	67°C isothermal
Injection port temperature:	150°C
Detector temperature:	300°C
Sample injection volumn:	3 µl

Figure 2-1 shows the separation achieved by the column.

7. The external standard method using integrated peak areas is used for quantification.

   a. Prepare a stock chloroform standard at 500 ng/µl in nanograde acetone.
   b. Prepare from the stock standard, a secondary chloroform standard at 5 ng/µl in methycyclohexane.
   c. Prepare from the secondary standard, seven calibration standards in methycyclohexane at concentrations of 50 ng/ml, 100 ng/ml, 500 ng/ml, 1000 ng/ml, 1500 ng/ml, 2000 ng/ml, and 2500 ng/ml.

d. Run a linear regression analysis on the seven calibration points and record the slope, y-intercept, and correlation coefficient.

e. Calculate the chloroform concentration in the unknown samples from:

$$\text{conc. (ng/ml)} = \frac{y-b}{m}$$

where:

y = integrated area of chloroform in unknown
b = y-intercept from linear regression analysis
m = slope from linear regression analysis

8. QA/QC

a. Generate and check calibration curves daily to confirm the linear range of the system.

b. Extract and analyze daily at least two aqueous standards (high and low concentration) in the same manner as the unknowns.

c. Analyze and monitor method blanks daily. The method blank consists of an aliquot of RO water treated in the same manner as the unknown.

F. Method Evaluation

1. Linearity

Figure 2-2 is a typical calibration curve from seven chloroform standards ranging from 50 ng/ml to 2500 ng/ml.

2. Accuracy and Precision

To determine the accuracy and precision of this method, aqueous chloroform standards were prepared in triplicate at seven concentrations ranging from 50 ng/ml to 2500 ng/ml. Each standard was extracted and analyzed in the same manner as samples. The results are given in Table 2-1.

Throughout the duration of this project, between 2 and 7 aqueous standards were analyzed on each day of sample analysis. Results as a function of time and concentration are given in Table 2-2.

For both the daily and long term, method accuracy is represented by the deviation of the mean recovery from 100%. The precision of the method is represented by the standard deviation and coefficient of variation of the average of the spiked recoveries.

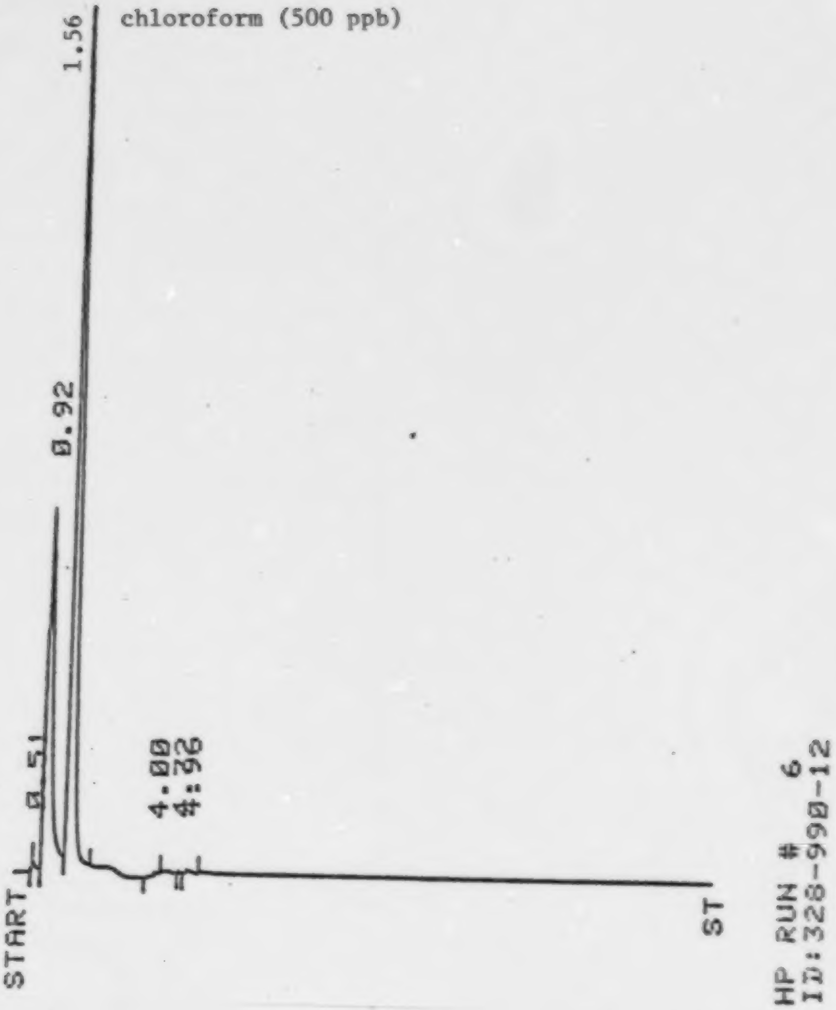

Figure 2-1. GC/EC chromatogram of chloroform. Column: 6 ft x 2 mm, 10% Squalane on Chromosorb WAW (80/100 mesh), 67°C isothermal.

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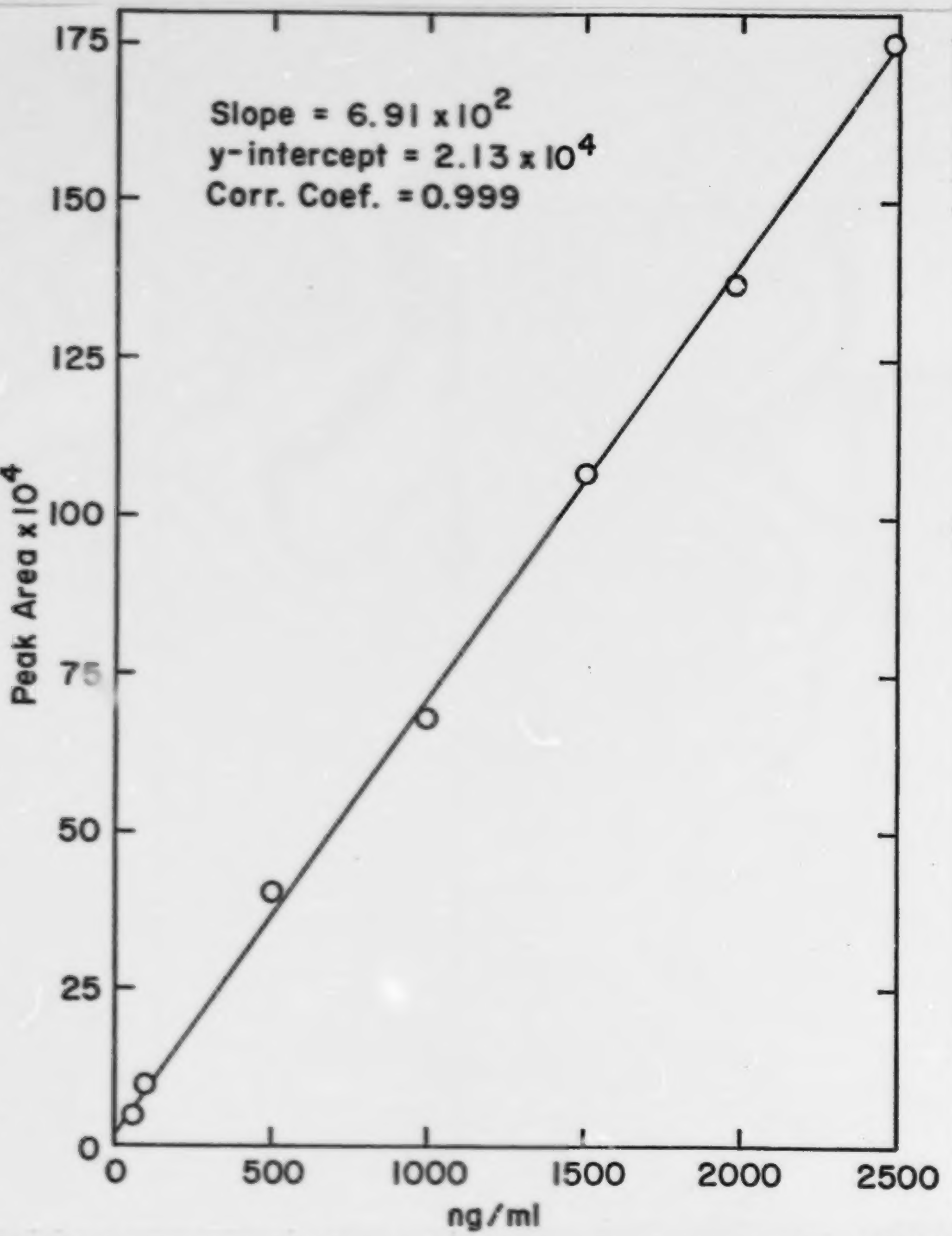

Figure 2-2. Integrated peak area versus chloroform concentration. GC/EC, column: 10% Squalane on Chromosorb WAW (80/100 mesh).

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TABLE 2-1. GROUP 2 - CHLOROFORM: ACCURACY AND PRECISION DATA FOR THE LIQUID/LIQUID EXTRACTION GC/EC ANALYTICAL METHOD

Concentration (ppm)	$\overline{\text{R.T.}}$ (min)	% Recovery mean	±	S.D.	(CV)
50	1.55	88	±	2	(2%)
100	1.56	95	±	3	(3%)
250	1.55	116	±	5	(4%)
500	1.55	116	±	5	(4%)
1000	1.55	102	±	4	(4%)
1500	1.55	101	±	4	(4%)
2500	1.55	99	±	3	(3%)

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TABLE 2-2. GROUP 2 - CHLOROFORM: ACCURACY AND PRECISION DATA FOR THE LIQUID/LIQUID EXTRACTION GC/EC ANALYTICAL METHOD

Concentration of Sample Spike (ppb)	Date Analyzed	% Recovery of Spike
50	10/05/81	66
500	10/05/81	77
500	10/08/81	95
1,000	10/08/81	102
2,500	10/08/81	95
500	10/15/81	92
1,000	10/15/81	98
2,500	10/15/81	87
500	10/26/81	88
1,500	10/26/81	100
2,500	10/26/81	100
50	11/03/81	40
1,000	11/03/81	93
50	12/01/81	116
500	12/01/81	90
1,500	12/01/81	79
50	12/30/81	58
500	12/30/81	104
1,500	12/30/81	97
2,500	12/30/81	87
50	02/10/82	89
500	02/10/82	86
50	03/12/82	86
100	03/12/82	98
250	03/12/82	95
500	03/12/82	96
1,000	03/12/82	96
1,500	03/12/82	95
2,500	03/12/82	84
50	04/01/82	99
100	04/01/82	99
250	04/01/82	100
500	04/01/82	95
1,000	04/01/82	92
1,500	04/01/82	93
2,500	04/01/82	88
		mean ± S.D. (CV)
		90 ± 13 (14%)

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APPENDIX I

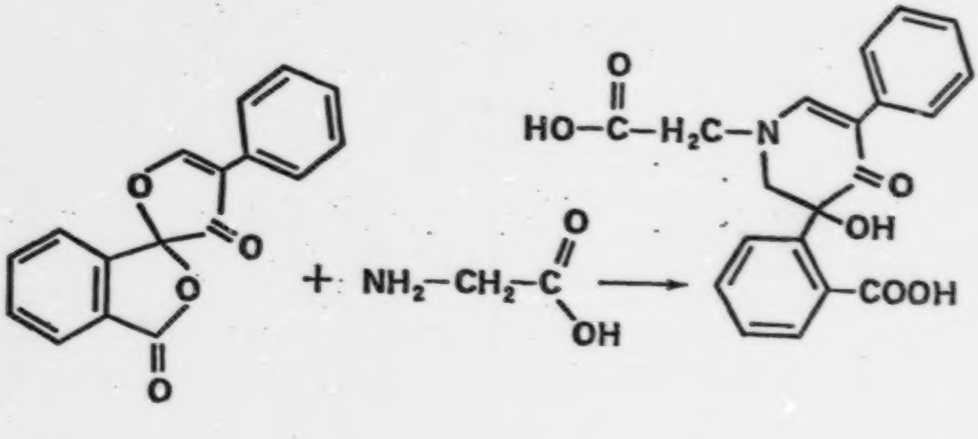
STANDARD OPERATING PROCEDURE FOR
GROUP 3: GLYCINE

A. Scope and Application

This method is applicable to the determination of glycine in an aqueous matrix over the concentration range 50 ng/ml to 2500 ng/ml. There is no interference from the other 21 compounds of interest in this study or from the acetone used to dissolve the primary stock RO spiking standards. However, aqueous samples with salts at a concentration greater than 0.5M will cause an irreversible change in the chromatographic properties of the C18 column and destroy the needed resolution.

B. Summary of Method

The aqueous sample containing glycine is buffered to pH 9 with sodium borate then reacted with the fluorogenic reagent Fluram, 4-phenylspiro [furan-2(3H), 1'-phthalan]-3,3'-dione to form an intensely fluorescent derivative. Figure 3-1 illustrates chromatograms resulting from the use of this method.



Fluram

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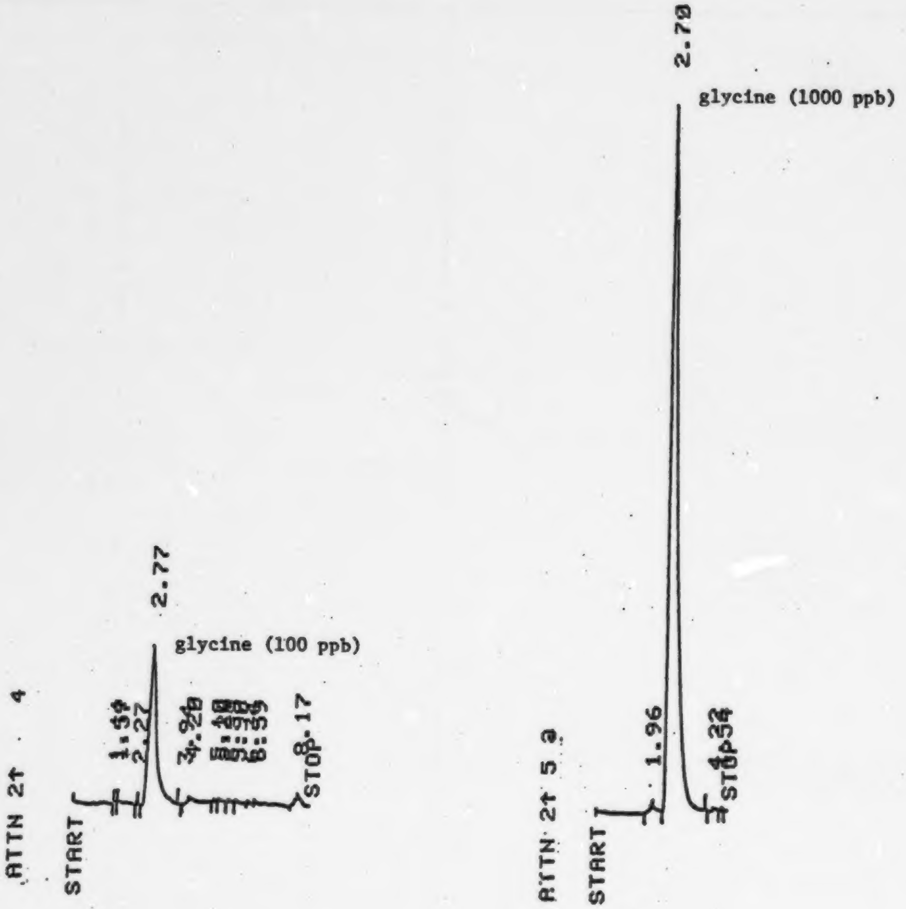

Figure 3-1. Fluram derivitization/HPLC/fluorescence chromatogram of glycine. C_{18} column, mobile phase: 50% CH_3CN/50% H_2O, flow: 1.0 ml/min.

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The derivatization agent is nonfluorescent, and any excess Fluram is hydrolyzed to form nonfluorescent, water soluble products (Roche Diagnostics). The resultant fluorophore is stable up to 30 minutes and is analyzed by reverse phase HPLC with a fluorescent detector (C18 column; acetonitrile/water mobile phase). Quantification is based on calibration by external standards.

C. Apparatus and Materials

1. Vortex mixer (#8929W, Arthur H. Thomas Co.)

2. High performance liquid chromatograph (Waters Model 660 solvent programmer with Model U6K injector) interfaced to variable excitation wavelength spectrofluorometer (Schoeffel FS970) with a means for automatic peak integration (HP 3385A Automatic System or Spectra-Physics SP4100 Computing Integrator).

3. Analytical column: 4 mm x 30 cm M-C18 (Waters) plus corresponding guard column.

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D. Reagents

1. Water, HPLC grade

2. Acetonitrile, HPLC grade

3. Fluram (Pierce Chemical Company)

4. Sodium borate (ACS, Baker)

E. Procedure

1. To prepare derivative:

    a. Place a 1 ml aliquot of sample into a 3-5 ml vial.
    b. Add 500 µl of pH 9 sodium borate buffer (7.6 g of $Na_2B_4O_7 \cdot 10H_2O$ diluted to 100 ml with HPLC grade water).
    c. While mixing the buffered solution on a vortex mixer, add 500 µl of 0.2 mg/ml Fluram (0.208 g Fluram diluted to 100 ml with HPLC grade acetonitrile).
    d. Mix for 1.0 min.
    e. Analyze the sample within 30 min after derivatization.

2. To analyze derivative: Analyze the derivatized sample by reverse phase HPLC/fluorescence detection. Instrument conditions are as follows.

Instrument: Waters HPLC (Model 660 solvent programmer with Model U6K injector) interfaced to a Schoeffel FS970 Spectrofluoro-

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monitor and either a HP 3385A Automation System or Spectra-Physics SP4100 Computing Integrator.

Analytical Column:	4 mm x 30 cm M-C18 (Waters) plus corresponding guard column.
Excitation wavelength:	390 nm
Emission filter:	470 nm
Mobile phase:	50% water + 50% acetonitrile, isocratic
Flow rate:	1.0 ml/min
Injection volume:	50 µl

3. The external standard method with integrated peak areas is used for quantification.

   a. Prepare a stock glycine standard at 10,000 ppm in HPLC grade water.
   b. Prepare calibration standards in HPLC grade water at concentrations of 50 ng/ml, 100 ng/ml, 250 ng/ml, 1000 ng/ml, 2500 ng/ml.
   c. Derivatize and analyze the aqueous calibration standards in the same manner as the unknowns.
   d. Run a linear regression analysis on the five calibration points and record the slope, y-intercept, and correlation coefficient.
   e. Calculate the glycine concentration in the unknown samples from:

$$\text{conc. (ng/ml)} = \frac{\underline{y-b}}{m}$$

where:

y = integrated area of glycine in unknown
b = y-intercept from linear regression analysis
m = slope from linear regression analysis

4. QA/QC

   a. Calibration curves should be generated and checked daily to confirm the linear response range of the system.
   b. Analyze and monitor method blanks daily. Use a derivatized aliquot of distilled water as the method blank. Subtract any interference area counts from standards and samples.
   c. Analyze a spiked sample for each group of five unknowns.

F. Method Evaluation

1. Linearity and Precision

Fortified distilled water samples were used to evaluate the linearity and precision of this method. Aqueous solutions were spiked with glycine at the following concentrations: 10 ng/ml, 50 ng/ml, 100 ng/ml, 1000 ng/ml, 1500 ng/ml, and 2500 ng/ml. Each concentration was derivatized in triplicate and analyzed with a corresponding distilled water blank. Table 3-1 indicates the method precision, and Figure 3-2 the method linearity. The method is precise and linear in the 50 ng/ml to 2500 ng/ml concentration range.

2. Accuracy and Precision

Throughout the duration of this project, samples spiked at various glycine concentration levels were analyzed. Results as a function of time and concentration are given in Table 3-2. Method accuracy is represented by the deviation of the mean recovery from 100%. The precision of the method over time is represented by the standard deviation and coefficient of variation of the spiked recoveries.

TABLE 3-1. GROUP 3: GLYCINE - CALIBRATION PRECISION DATA FOR THE FLURAM DERIVATIZATION/HPLC/FLUORESCENCE ANALYTICAL METHOD

Glycine Concentration	$\overline{\text{R.T.}}$ (min)	Area Counts Mean	±	S.D.	(% CV)
10 ppb	2.76	1208	±	372	(31)
50 ppb	2.71	4384	±	756	(17)
100 ppb	2.70	7331	±	1082	(15)
1000 ppb	2.69	71813	±	1871	(3)
1500 ppb	2.70	102013	±	6213	(6)
2500 ppb*	2.53	166930	±	5900	(4)

*injection volume 5 µl; 50 µl for other concentrations

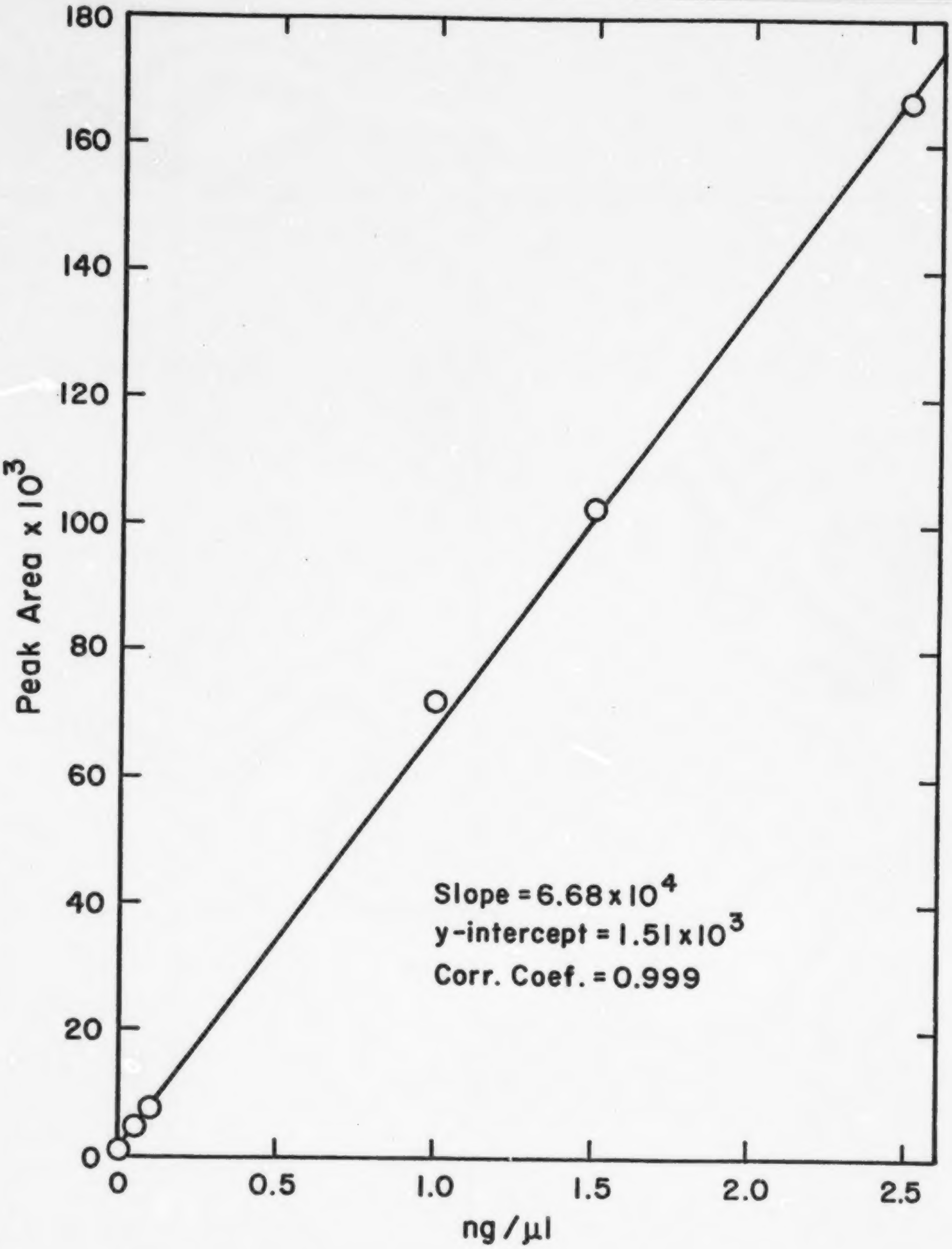

Figure 3-2. Integrated peak area versus glycine concentration. Fluram derivatization/HPLC/fluorescence, λex >390 nm, λem 470 nm, mobile phase: 85% CH_3CN/15% H_2O, column C18.

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TABLE 3-2. GROUP 3 - GLYCINE: ACCURACY AND PRECISION DATA FOR THE FLURAM DERIVATIZATION/HPLC/FLUORESCENCE ANALAYTICAL METHOD

Concentration of Sample Spike	Date Analyzed	% Recovery of Spike
2441	10/27/81	100
1018	10/27/81	100
1018	10/27/81	100
2441	11/03/81	103
2525	04/28/82	99
253	04/28/82	100
1010	04/29/82	107
1010	04/29/82	108
101	04/30/82	115
255	04/30/82	103
255	04/30/82	116
252	05/03/82	126
252	05/03/82	113
252	05/04/82	113
252	05/04/82	93
	mean ± S.D. (CV)	106 ± 9 (8%)

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APPENDIX J

STANDARD OPERATING PROCEDURE FOR GROUP 4: GLUCOSE

A. Scope and Application

This method is applicable to the determination of ^{14}C-glucose in an aqueous matrix over the concentration range 1 ng/ml to 2500 ng/ml. There is no interference from the other compounds in this study, and there are no matrix problems.

B. Summary of Method

Carbon 14 radiolabeled glucose is diluted with pure glucose to prepare an aqueous solution of known specific activity which is then added to the system matrix prior to making a concentration run. An aliquot of the aqueous solution is used as a standard for recovery determinations. Sample aliquots and standard aliquots are mixed with a scintillation counting cocktail and counted in a liquid scintillation spectrometer. Standard and sample count rates are integrated and corrected for counting efficiency. Glucose recovery is calculated from corrected absolute count rates and specific activity of the starting solution.

C. Apparatus and Material

1. Scintillation vials.
2. Liquid scintillation spectrometer (LSC) (Beckman LSC-7500).
3. Proper laboratory areas and safety equipment to handle radiolabeled materials.

D. Reagents

1. Liquid scintillation cocktail (Beckman MP).
2. D-(4)-Glucose (Aldrich).
3. ^{14}C-D-Glucose (New England Nuclear).

E. **Procedure**

1. Spike glucose into the RO system as a mixture of cold and ^{14}C-glucose. This mixture is prepared by diluting 83 µCi[^{14}C] glucose with 8.4 mg unlabeled glucose in 10 ml of deionized, distilled water. 10 µl of the resulting solution is added to 5 ml of water for use as a counting standard.

2. Collect 5 ml sample aliquots at suitable times and sampling points during the concentration run.

3. Place a 5 ml sample aliquot and 10 ml LSC counting cocktail in a scintillation vial.

4. Shake vigorously for 20 seconds.

5. Place the samples in an LSC.

6. Standardize the counter with a NBS traceable unquenched ^{14}C counting standard, following the procedure outlined in the LSC operating manual.

7. Count the samples for 10 min or to 1% accuracy.

8. After counting, spike each sample with 1 µl of a known ^{14}C-glucose standard containing approximately 21787 cpm.

9. Recount samples and a blank spiked in the same manner as the samples.

10. Calculate the counting efficiency for each individual sample:

$$\text{Efficiency (E)} = \frac{\text{CPM}_{(\text{step 9})} - \text{CPM}_{(\text{step 7})}}{\text{CPM spiked}_{(\text{step 8})}}$$

11. Calculate the glucose concentration in the unknown samples:

$$\text{conc } (\mu\text{g/ml}) = \frac{\text{CPM}}{\text{E}} \times \frac{1}{5\text{ml}} \times \frac{\mu\text{g}}{\text{dpm}}$$

where:

µg/dpm is calculated as follows:

$$\frac{\text{wt. glucose (mg)}}{\text{dpm}} \times \frac{1000\ \mu\text{g}}{1\ \text{mg}} = \mu\text{g/dpm}$$

the wt. glucose is the combined weight of unlabeled and labeled glucose used in the experiment.

12. QA/QC

Quality control is monitored by daily calibration of the LSC using

NBS traceable standard unquenched ^{14}C in a sealed counting vial. Further quality assurance is monitored by determination of sample matrix effects by spiking each sample with ^{14}C labeled glucose standards to eliminate sample matrix effects. Table 4-1 is a summary of quality control data and demonstrates the efficiency for all analyses on the date given.

TABLE 4-1. Group 4 - GLUCOSE: DAILY METHOD EFFICIENCY

Date Analyzed					
02/09/82		03/10/82		03/24/32	
Sample Concentration (ppb)	Efficiency (%)	Sample Concentration (ppb)	Efficiency (%)	Sample Concentration (ppb)	Efficiency (%)
0	104	0	97	0	91
40	109	12	90	26	93
0	91	0	88	0	56
8.4	96	1.2	99	0.9	100
0	108	0	93	0	99
220	105	240	90	230	79
140	101	130	88	130	93
150	92	130	93	130	84
8.7	93	19	91	17	84
15	102	1.5	89	1.6	101
400	90	430	99	330	62
480	106	440	86	420	95
	mean ± S.D. (CV) 100 ± 7 (7%)		mean ± S.D. (CV) 92 ± 4 (4%)		mean ± S.D. (CV) 86 ± 15 (17%)

APPENDIX K

STANDARD OPERATING PROCEDURE FOR
GROUP 5: TRIMESIC ACID

A. Scope and Application

This method is applicable to the determination of trimesic acid in an aqueous matrix over the concentration range 50 ng/ml to 2500 ng/ml. There is no interference from the other 21 compounds of interest to this study or from the acetone used to dissolve the primary stock RO spiking standards. However, aqueous samples with salts at a concentration greater than 0.5M will cause an irreversible change in the chromatographic properties of the C18 column and destroy the needed resolution.

B Summary of Method

An aliquot of the aqueous sample is injected and analyzed by reverse phase HPLC with a variable wavelength UV detector. A C18 column with a acetonitrile/water mobile phase provides the needed separation, and detection at $\lambda = 220$ nm provides the needed sensitivity. Quantification is based on calibration by external standards.

C. Apparatus and Materials

1. High performance liquid chromatograph (Waters Model 660 solvent programmer with Model U6K injector) interfaced to a variable wavelength UV detector (Perkin-Elmer LC-75 spectrophotometric detector) with a means for automatic peak integration (HP 3385A Automation System or Spectra-Physics SP4100 Computing Integrator).

2. Analytical column: 4 mm x 30 cm M-C18 (Waters) plus corresponding guard column.

D. Reagents

1. Water, HPLC grade

2. Acetonitrile, HPLC grade

E. Procedure

1. Ensure the sample pH is between 2 and 8.

2. Inject a 100 µl aliquot of the sample into the HPLC/UV system. (Samples that are cloudy or have suspended particulates should be filtered before injection). The instrument conditions are as follows:

Instrument:	Waters HPLC (Model 660 solvent programmer with Model U6K injector) interfaced with Perkin-Elmer LC-75 spectrophotometric detector and either a HP 3385A Automation System or Spectra-Physics SP4100 Computing Integrator.
Analytical column:	4 mm x 30 cm M-C18 (Waters) plus corresponding guard column.
Wavelength:	220 nm
Mobile phase:	5% acetonitrile + 95% water, isocratic
Flow rate:	1.0 ml/min
Injection volume:	100 µl

Figure 5-1 shows the separation achieved by the column.

3. The external standard method using integrated peak areas is used for quantification.

   a. Prepare a stock trimesic acid standard at 2500 µg/ml in nanograde acetone.
   b. Prepare, from the standard stock solution, five calibration standards in HPLC grade water at concentrations of 50 ng/ml, 100 ng/ml, 250 ng/ml, 1000 ng/ml, and 2500 ng/ml.
   c. Run a linear regression analysis on the five calibration points and record the slope, y-intercept, and correlation coefficient.
   d. Calculate the trimesic acid concentration in the unknown samples from:

$$\text{conc. (ng/ml)} = \frac{y-b}{m}$$

where:
y = integrated area of trimesic acid is unknown.
b = y-intercept from linear regression analysis.
m = slope from linear regression analysis.

4. QA/QC

   a. Calibration curves should be generated and checked daily to

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confirm the linear response range of the system.

b. Analyze and monitor method blanks daily. Use as a method blank an aliquot of the HPLC water used for standard dilutions. Subtract any interference area counts from standards and samples.

c. Analyze a spiked sample for each group of five unknowns.

F. Method Evaluation

1. Linearity and Precision

Fortified distilled water samples were used to evaluate the linearity and precision of this method. Aqueous solutions were spiked with trimesic acid at the following concentrations: 20 ng/ml, 50 ng/ml, 100 ng/ml, 500 ng/ml, 1000 ng/ml, and 2500 ng/ml. Each concentration was analyzed in triplicate, with a corresponding distilled water blank. Table 5-1 indicates the method precision, and Figure 5-2 the method linearity. The method is precise and linear in the 50 ng/ml to 2500 ng/ml concentration range.

2. Accuracy and Precision

Throughout this project samples spiked at various trimesic acid concentration levels were analyzed. Results as a function of time and concentration are given in Table 5-2. Method accuracy is represented by the deviation of the mean recovery from 100%. The precision of the method over time is represented by the standard deviation and coefficient of variation of the average of the spiked recoveries.

TABLE 5-1. GROUP 5 - TRIMESIC ACID: PRECISION DATA FOR THE HPLC/UV ANALYTICAL METHOD

Trimesic Acid Concentration	$\overline{\text{R.T.}}$ (min)	Area Counts Mean	±	S.D.	(% CV)
20 ppb	2.01	3740	±	834	(22)
50 ppb	1.96	6177	±	510	(8)
100 ppb	1.99	14723	±	626	(4)
500 ppb	1.97	51027	±	320	(1)
1000 ppb	1.99	97933	±	313	(0.3)
2500 ppb	1.99	247600	±	624	(0.3)

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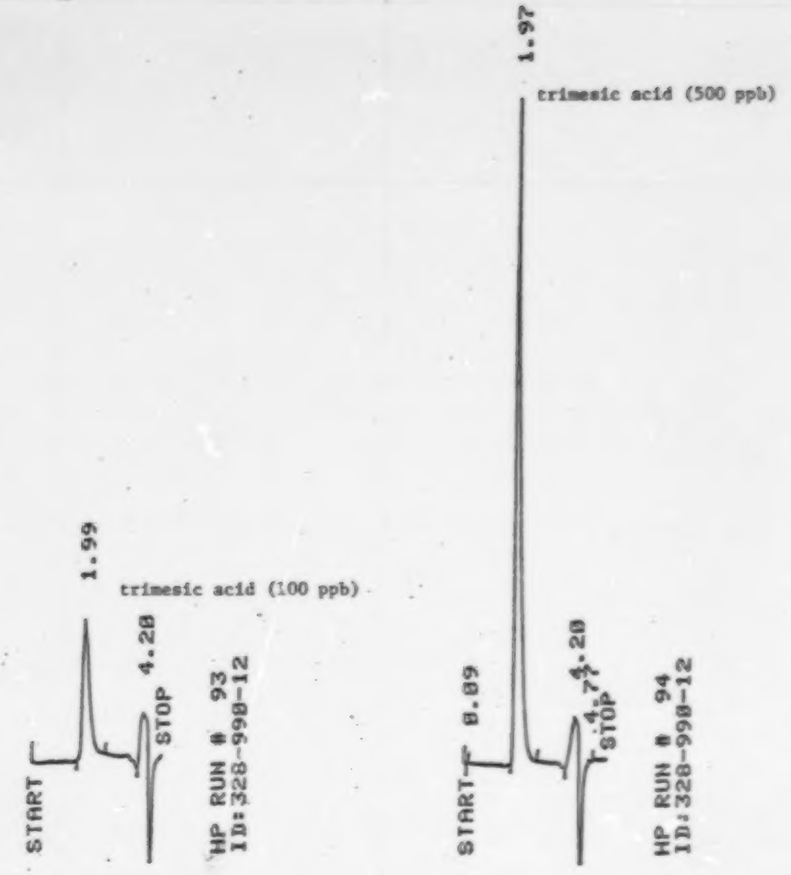

Figure 5-1. HPLC/UV chromatogram of trimesic acid. C18 column, mobile phase: 5% CH_3CN/95% H_2O, flow: 1.0 ml/min.

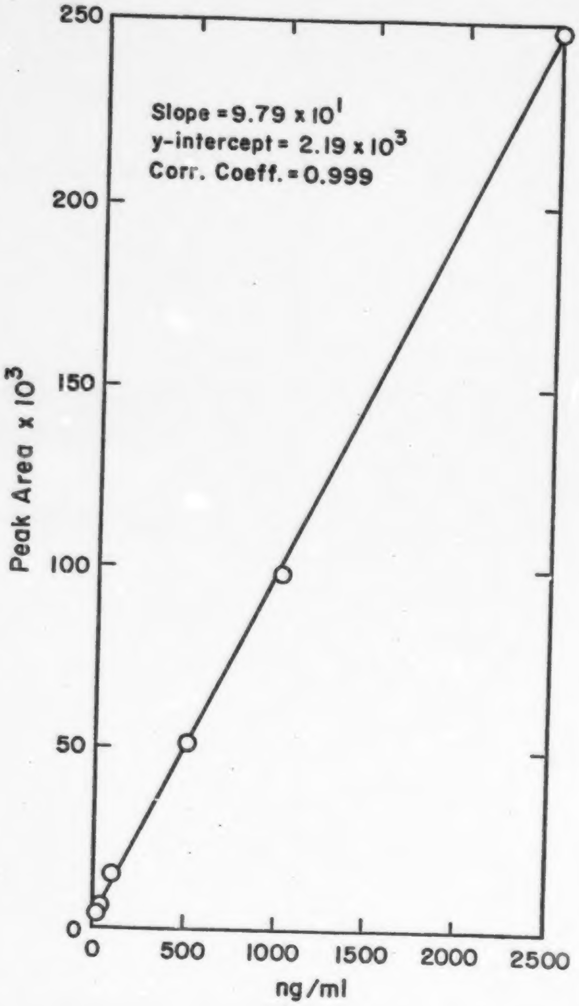

Figure 5-2. Integrated peak area versus trimesic acid concentration. HPLC/UV, λ 220 nm, mobile phase: 5% CH_3CN/95% H_2O, column C18.

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TABLE 5-2. GROUP 5 - TRIMESIC ACID: ACCURACY AND PRECISION DATA FOR THE REVERSE PHASE HPLC/UV ANALYTICAL METHOD

Concentration of Sample Spike	Date Analyzed	% Recovery of Spike
1006	10/09/81	94
1006	11/02/81	104
252	11/02/81	112
1006	11/02/81	111
1006	11/09/81	105
1000	01/05/82	96
1000	01/07/82	102
251	01/07/82	89
2505	01/07/82	93
251	01/07/82	115
		mean ± S.D. (CV) 102 ± 9 (9%)

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APPENDIX L

STANDARD OPERATING PROCEDURE FOR GROUP 6: FURFURAL

A. Scope and Application

The following two methods are both applicable to the determination of furfural in an aqueous matrix over the concentration range 50 ng/ml to 2500 ng/ml. Both methods are free from interference by the other 21 compounds of interest to this study or from the acetone used to dissolve the primary stock RO spiking standards. Except where specified, the standard operating procedure for both methods is the same.

Method 6-A can be used for routine analysis of samples with very low concentrations of salts (~100 ppm). Samples with very high salt concentrations will cause an irreversible change in the chromatographic properties of the C18 column and destroy the needed resolution.

Method 6-B is the method of choice for salt containing samples. This method has been shown to tolerate up to 1M salts by simply cleaning the column when needed. Increased pump pressure will indicate the need for column cleaning. To clean the column, backwash with 40% CH_3CN in 0.01N H_2SO_4 at 0.1 ml/min for at least 4 hours. Further backwash with 0.05N H_2SO_4 for an additional 4 hours to regenerate the column. The column can then be returned to operating conditions for further analysis.

B. Summary of Method

1. Method 6-A

An aliquot of the aqueous sample is injected and analyzed by reverse phase HPLC with a variable wavelength detector. A C18 column with an acetonitrile/water mobile phase provides the needed separation, and detection at $\lambda = 271$ nm provides the needed sensitivity.

2. Method 6-B

An aliquot of the aqueous sample is injected and analyzed by size exclusion HPLC with a variable wavelength detector. An Aminex HPX-85 column with a 0.01N H_2SO_4/acetonitrile mobile phase provides the needed separation, and detection at $\lambda = 271$ nm provides the needed sensitivity.

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For both methods, quantification is based on calibration by external standards.

C. Apparatus and Materials

1. High performance liquid chromatograph (Waters Model 660 solvent programmer with Model U6K injector) interfaced to a variable wavelength UV detector (Perkin-Elmer LC 75 spectrophotometric detector) with a means for automatic peak integration (HP 3385A Automation System or Spectra-Physics SP4100 Computing Integrator).

2. Analytical column

Method 6-A:	30 cm x 4 mm M-C18 (Waters) plus corresponding guard column (Supelco)
Method 6-B:	25 cm x 4 mm Aminex HPX-85 with guard column Q15S B-19460 in H^+ form (Biorad)

D. Reagents

1. Method 6-A
   - a. Water, HPLC grade
   - b. Acetonitrile, HPLC grade
2. Method 6-B
   - a. Water, HPLC grade
   - b. 0.01N H_2SO_4 prepared from HPLC grade water
   - c. Acetonitrile, HPLC grade.

E. Procedure

1. Method 6-A
   - a. Ensure sample pH is between 2 and 8
   - b. Inject a 150 μl aliquot of the sample into the HPLC/UV system. (Samples that are cloudy or have suspended particulates should be filtered before injection.) The instrument conditions are as follows.

Instrument model:	Waters HPLC (Model 660 solvent programmer with U6K injector) interfaced with Perkin-Elmer LC-75 spectrophotometric detector and either a HP 3385A Automation System or Spectra-Physics SP4100 Computing Integrator

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Analytical column: 30 cm x 4 mm M-C18 (Waters) plus corresponding guard column

Wavelength: 271 nm

Mobile phase: 94% water + 6% acetonitile, isocratic

Flow rate: 0.9 ml/min

Injection volume: 150 µl

Figure 6-1 shows the separation achieved by the C18 column.

2. Method 6-B

a. Adjust the sample to pH 2 with dilute H_2SO_4.
b. Inject a 100 µl aliquot of the sample into the HPLC/UV system. (Samples that are cloudy or have suspended particulates should be filtered before injection.) The instrument conditions are as follows.

Instrument: Waters HPLC (Model 660 solvent programmer with Model U6K injector) interfaced with Perkin-Elmer LC-75 spectrophotometric detector and either a HP 3385A Automation System or Spectra-Physics SP4100 Computing Integrator

Analytical column: 25 cm x 4 mm Aminex HPX-85

Guard column: Q15S B-19460 in H^+ form

Wavelength: 271 nm

Mobile phase: 73% 0.01N H_2SO_4 + 27% acetonitrile, isocratic

Flow rate: 0.3 ml/min

Injection volume: 100 µl

Figure 6-2 shows the separation achieved by the Aminex HPX-85 column.

3. For both methods, the external standard method using integrated peak areas is used for quantification.

a. Prepare a stock furfural standard at 500 µg/ml in nanograde acetone.
b. Prepare, from the standard stock solution, five calibration standards in HPLC grade water at concentrations of 50 ng/ml, 100 ng/ml, 250 ng/ml, 1000 ng/ml, and 2500 ng/ml.

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c. Run a linear regression analysis on the five calibration points and record the slope, y-intercept, and correlation coefficient.

d. Calculate the furfural concetration in the unknown samples from:

$$\text{conc. (ng/ml)} = \frac{y-b}{m}$$

where:

y = integrated area of furfural in unknown
b = y-intercept from linear regression analysis
m = slope from linear regression analysis

4. QA/QC

a. Calibration curves should be generated and checked daily to confirm the linear response range of the system.

b. Analyze and monitor method blanks daily. Use as a method blank an aliquot of the HPLC water used for standard dilutions. Subtract any interference area counts from standards and samples.

c. Analyze a spiked sample for each group of five unknowns.

F. Method Evaluation

1. Linearity and Precision

Fortified distilled water samples were used to evaluate the linearity and precision of methods 6-A and 6-B. Aqueous solutions were spiked with furfural at five concentrations ranging from 50 ng/ml to 2500 ng/ml. Each concentration was analyzed in triplicate with a corresponding distilled water blank. Table 6-1 indicates the method precision for methods 6-A and 6-B. Figures 6-3 and 6-4 show the method linearity for methods 6-A and 6-B, respectively.

2. Accuracy and Precision

Throughout this project, samples spiked at various furfural concentrations were analyzed. Method 6-A was initially used, but problems associated with salt containing samples led to the development and use of Method 6-B. Results as a function of time and concentration for both methods are given in Table 6-2. Method accuracy is represented by the deviation of the mean recovery from 100%. The precision of the method over time is represented by the standard deviation and coefficient of variation of the average of the spiked recoveries.

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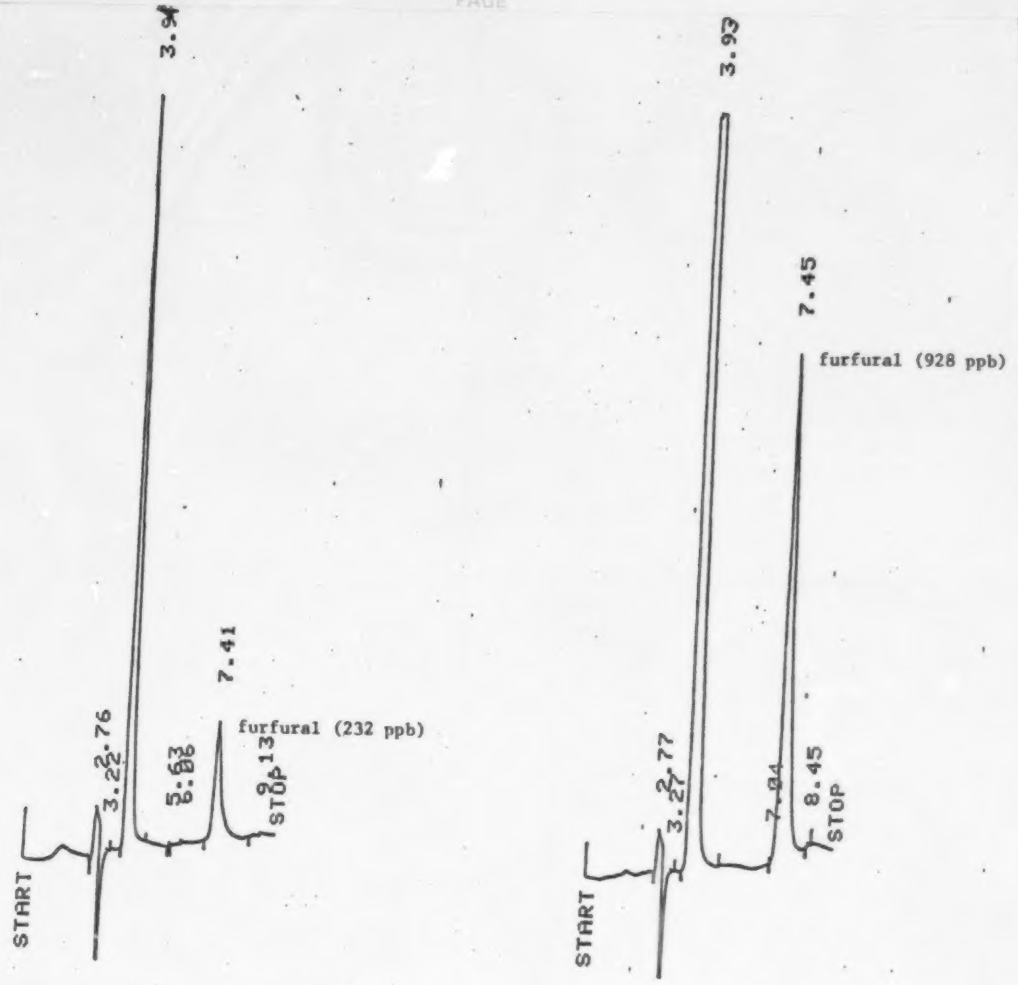

Figure 6-1. HPLC/UV chromatogram of furfural, Method 6-A. C18 column, mobile phase: 94% H_2O/6% CH_3CN, flow: 0.9 ml/min.

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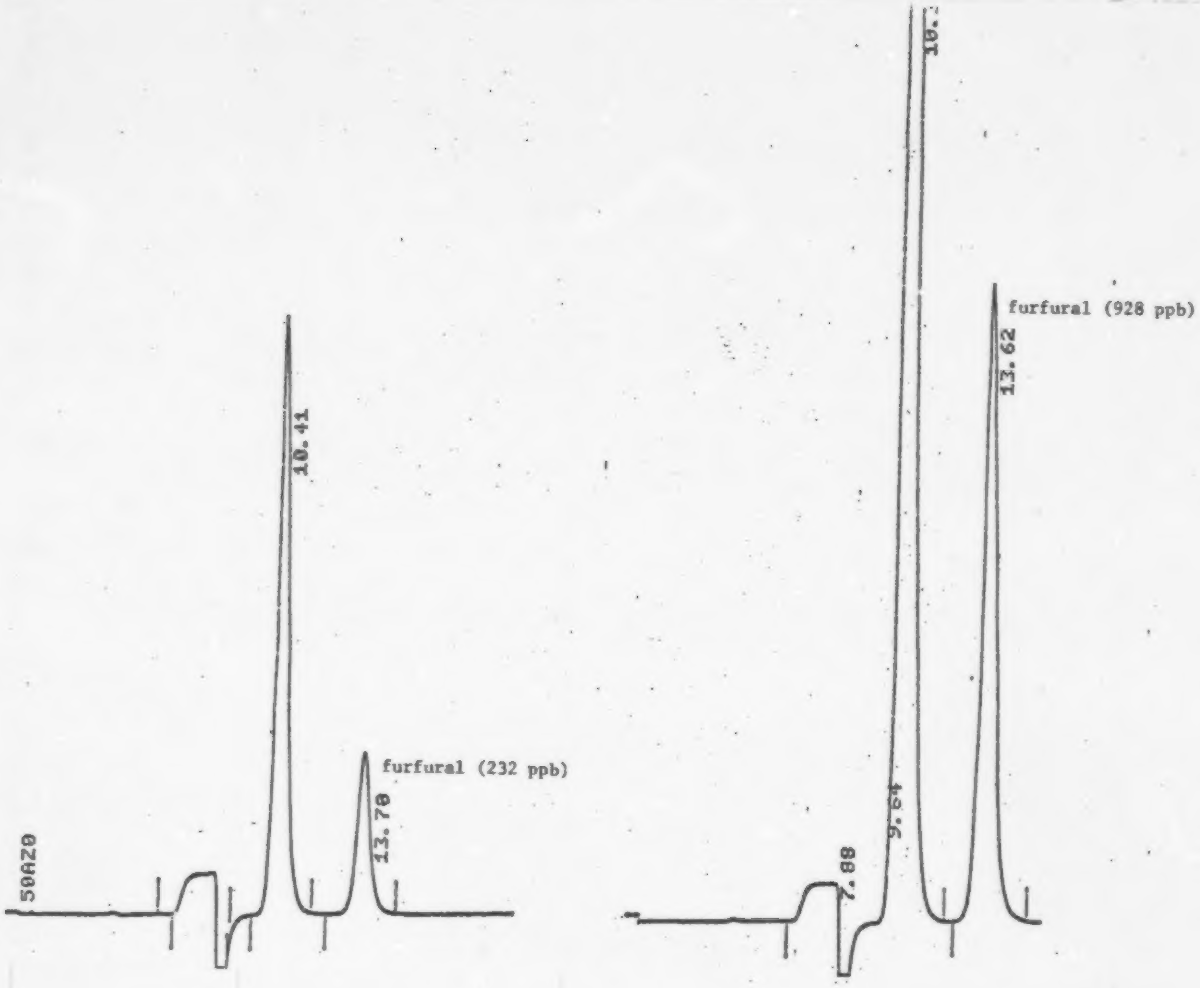

Figure 6-2. HPLC/UV chromatogram of furfural, Method 6-B. Column: Aminex HPX-85, mobile phase: 73% 0.01 N H_2SO_4/27% CH_3CN, flow: 0.3 ml/min.

TABLE 6-1. GROUP 6-A and 6-B - FURFURAL: PRECISION DATA FOR THE REVERSE PHASE AND SIZE EXCLUSION HPLC/UV ANALYTICAL METHODS

Method	Furfural Concentration (ppb)	$\overline{\text{R.T.}}$ (min)	Area Counts Mean	±	S.D.	(% CV)
6-A	46	7.41	2483	±	223	(9)
	93	7.41	3768	±	117	(3)
	232	7.38	12891	±	760	(6)
	928	7.39	52085	±	1477	(3)
	2320	7.36	136381	±	579	(0.4)
6-B	46	14.7	84432	±	4782	(6)
	93	14.0	137452	±	3828	(3)
	232	13.7	358742	±	1464	(0.4)
	928	13.6	1453756	±	4650	(0.3)
	2320	13.7	3569604	±	11437	(0.3)

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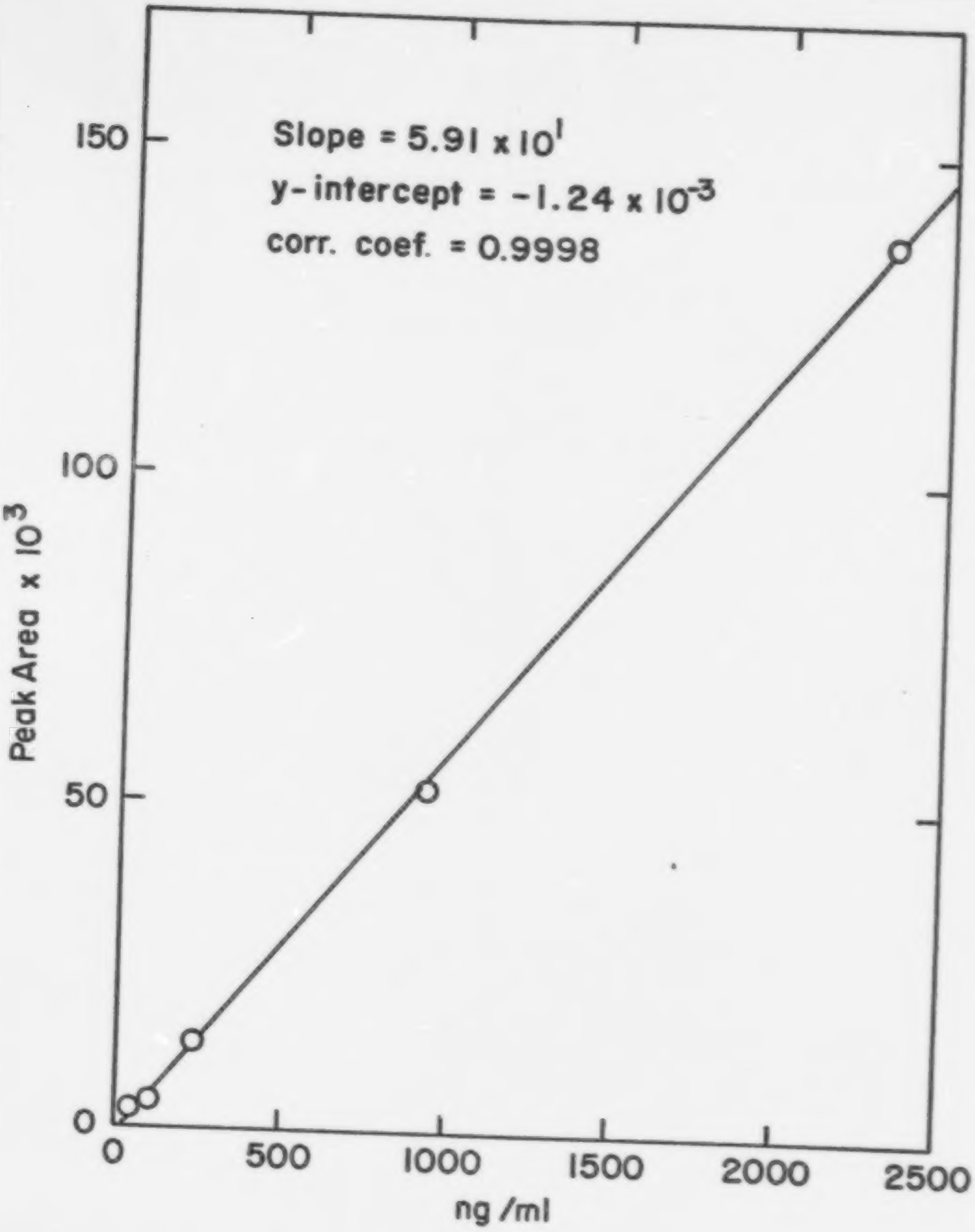

Figure 6-3. Integrated peak area versus furfural concentration, Method 6-A. HPLC/UV, 271 nm, mobile phase: 94% H_2O/6% CH_3CN, column C18.

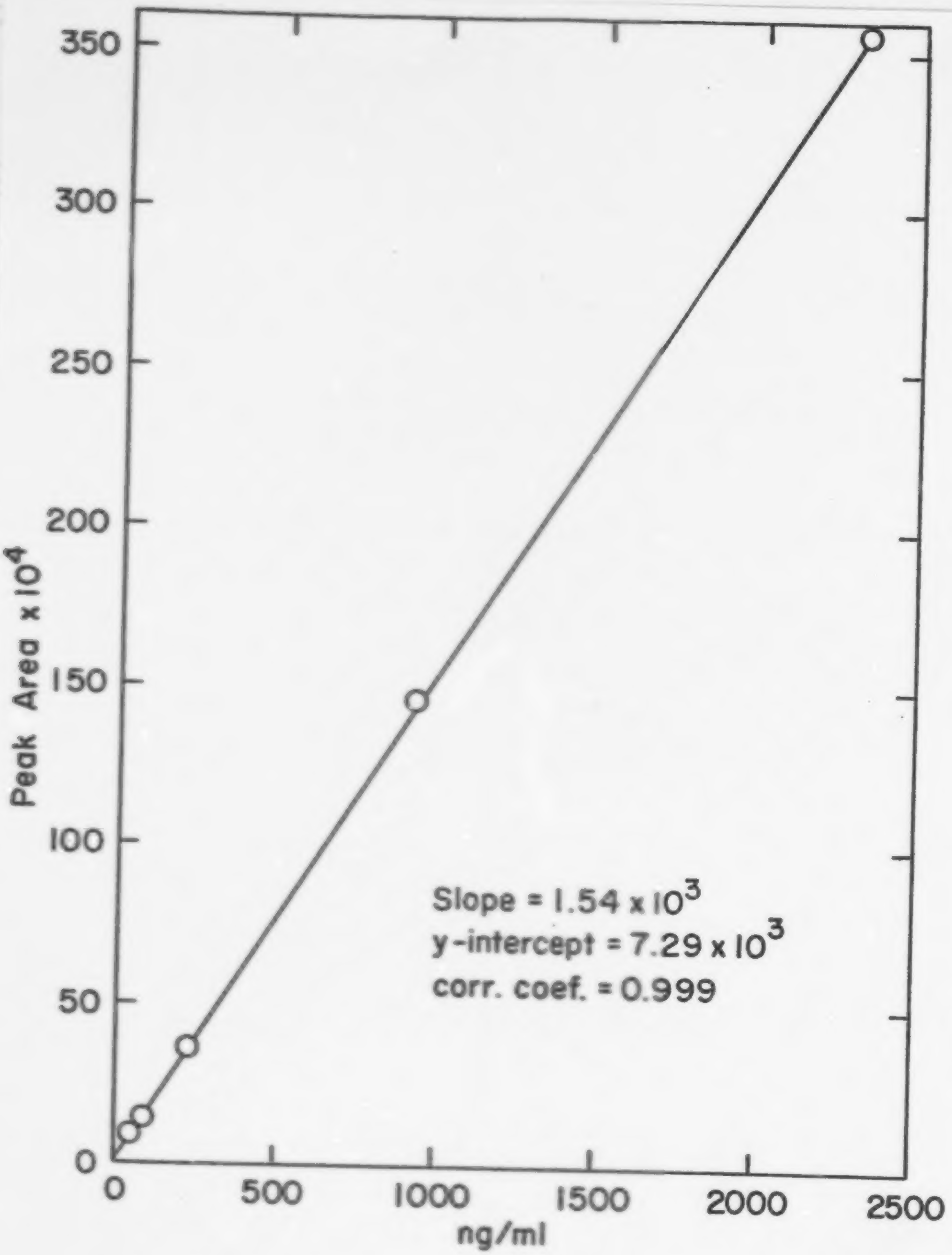

Figure 6-4. Integrated peak area versus furfural concentration, Method 6-B. HPLC/UV, 271 nm, mobile phase 73% 0.01 N H_2SO_4/27% CH_3CN, column: Aminex HPX-85.

TABLE 6-2. GROUP 6-A and 6-B - FURFURAL: ACCURACY AND PRECISION FOR THE REVERSE PHASE AND SIZE EXCLUSION HPLC/UV ANALYTICAL METHODS

Method	Concentration of Sample Spike	Date Analyzed	% Recovery of Spike
6-A	232	10/13/81	107
6-A	232	10/26/81	98
6-A	928	10/30/81	97
6-A	232	10/30/81	102
6-A	255	12/07/81	101
6-A	1020	12/07/81	101
6-A	102	12/07/81	86
6-A	279	01/08/82	99
6-A	111	01/11/82	82
6-A	279	01/11/82	80
6-A	279	01/11/82	85
			mean ± S.D. (CV) 94 ± 9 (10%)
6-B	928	03/01/82	105
6-B	232	03/01/82	101
6-B	928	03/03/82	97
6-B	232	03/15/82	102
6-B	232	03/15/82	98
6-B	278	03/24/82	95
6-B	278	03/24/82	102
			mean ± S.D. (CV) 100 ± 3 (3%)

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APPENDIX M

STANDARD OPERATING PROCEDURE FOR GROUP 7: 5-CHLOROURACIL

A. Scope and Application

The following two methods are both applicable to the determination of 5-chlorouracil in an aqueous matrix over the concentration range 50 ng/ ml to 2500 ng/ml. Both methods are free from interference by the other 21 compounds of interest to this study or from the acetone used to dissolve the primary stock RO spiking standards. Except where specified, the standard operating procedure for both methods is the same.

Method 7-A can be used for routine analysis of samples with very low concentrations of salts (<100 ppm). Samples with salt concentrations >100 ppm will cause an irreversible change in the chromatographic properties of the C18 column and destroy the needed resolution.

Method 7-B is the method of choice for salt containing samples. This method has been shown to tolerate up to 1M salts by simply cleaning the column when needed. Increased pump pressure will indicate the need for column cleaning. To clean the column, backwash with 40% CH_3CN in 0.01N H_2SO_4 at 0.1 ml/min for at least 4 hours. Further backwash with 0.05N H_2SO_4 for an additional 4 hours to regenerate the column. The column can then be returned to operating conditions for further analysis.

B. Summary of Method

1. Method 7-A

An aliquot of the aqueous sample is injected and analyzed by reverse phase HPLC with a variable wavelength detector. A C18 column with a methanol/water mobile phase provides the needed separation (1), and detection at $\lambda = 272$ nm provides the needed sensitivity.

2. Method 7-B

An aliquot of the aqueous sample is injected and analyzed by size exclusion HPLC with a variable wavelength detector. An Aminex HPX-85 column

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1. B. Grathorne, C.D. Watts, and M. Fielding, J. Chromatog. 185 (1979) 671-690.

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with a 0.01N H_2SO_4 mobile phase provides the needed separation and detection at $\lambda = 272$ nm provides the needed sensitivity.

For both methods quantification is based on calibration by external standards.

C. Apparatus and Materials

1. High performance liquid chromatograph (Waters Model 660 solvent programmer with Model U6K injector) interfaced to a variable wavelength UV detector (Perkin-Elmer LC 75 spectrometric detector) with a means for automatic peak integration (HP 3385A Automation System or Spectra-Physics SP4100 Computing Integrator).

2. Analytical column

Method 7-A:	30 cm x 4 mm M-C18 plus corresponding guard column. (Waters)
Method 7-B:	25 cm x 4 mm Aminex HPX-85 with guard column Q15S B-19460 in H^+ form. (Biorad)

3. For Method 7-B only, capability to control the HPLC column temperature at 33.5°C.

D. Reagents

1. Method 7-A

   a. Water, HPLC grade
   b. Methanol, HPLC grade

2. Method 7-B

   a. Water, HPLC grade
   b. 0.01N H_2SO_4 prepared from HPLC grade water

E. Procedure

1. Method 7-A

   a. Ensure sample pH is between 2 and 8.
   b. Inject a 150 μl aliquot of the sample into the HPLC/UV system. (Samples that are cloudy or have suspended particulates should be filtered before injection.) The instrument conditions are as follows:

Instrument: Waters HPLC (Model 660 solvent programmer with Model U6K injector) interfaced with Perkin-Elmer LC-75 spectrophotometric detector and either a HP 3385A Automation System or Spectra-Physics SP4100 Computing Integrator.

Analytical column: 30 cm x 4 mm M-C18 (Waters) plus corresponding guard column.

Wavelength: 272 nm

Mobile phase: 8% methanol + 92% water, isocratic

Flow rate: 1 ml/min

Injection volume: 150 µl

Figure 7-1 shows the separation achieved by the C18 column.

2. Method 7-B

a. Adjust the sample to pH 2 with dilute H_2SO_4. (Dilute the H_2SO_4 with HPLC grade water.)

b. Inject a 100 µl aliquot of the sample into the HPLC/UV system. (Samples that are cloudy or have suspended particulates should be filtered before injection.) The instrument conditions are as follows:

Instrument: Waters HPLC (Model 660 solvent programmer with Model U6K injector) interfaced with Perkin-Elmer LC-75 spectrophotometric detector and either a HP 3385A Automation System or Spectra-Physics SP4100 Computing Integrator.

Analytical column: 25 cm x 4 mm Aminex HPX-85

Guard column: Q15S B-19460 in H^+ form

Column temperature: 33.5°C

Wavelength: 272 nm

Mobile phase: 0.01N H_2SO_4

Flow rate 0.5 ml/min

Injection volume: 100 µl

Figure 7-2 shows the separation achieved by the Aminex HPX-85 column.

3. For both methods, the external standard method using integrated peak areas is used for quantification.

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a. Prepare a stock 5-chlorouracil standard at 10 µg/ml in HPLC grade water.

b. Prepare, from the standard stock solution, five calibration standards in HPLC grade water at concentrations of 50 ng/ml, 100 ng/ml, 250 ng/ml, 1000 ng/ml, and 2500 ng/ml.

c. Run a linear regression analysis on the five calibration points and record the slope, y-intercept, and correlation coefficient.

d. Calculate the 5-chlorouracil concentration in the unknown samples from:

$$\text{conc. (ng/ml)} = \frac{y-b}{m}$$

where:

y = integrated area of 5-chlorouracil in unknown
b = y-intercept from linear regression analysis
m = slope from linear regression analysis.

4. QA/QC

a. Generate and check calibration curves daily to confirm the linear response range of the system.

b. Analyze and monitor method blanks daily. Use as a method blank an aliquot of the HPLC water used for standard dilutions. Subtract any area counts for interferences from standards and samples.

c. Analyze a spiked sample for each group of five unknowns.

F. Method Evaluation

1. Linearity and Precision

Fortified distilled water samples were used to evaluate the linearity and precision of Methods 7-A and 7-B. Aqueous solutions were spiked with 5-chlorouracil for at least five concentrations ranging from 20 ng/ml to 2500 ng/ml. Each concentration was analyzed in triplicate with a corresponding distilled water blank. Table 7-1 indicates the method precision for Methods 7-A and 7-B. Figures 7-3 and 7-4 show the method linearity for Methods 7-A and 7-B, respectively.

2. Accuracy and Precision

Throughout this project samples spiked at various 5-chlorouracil concentrations were analyzed. Method 7-A was used initially, but problems associated with salt-containing samples led to the development and use of Method 7-B. Results as a function of time and concentration for both methods are given in Table 7-2. Method accuracy is represented by the deviation of the mean recovery from 100%. The precision of the method over time is represented by the standard deviation and coefficient of variation of the average of the spiked recoveries.

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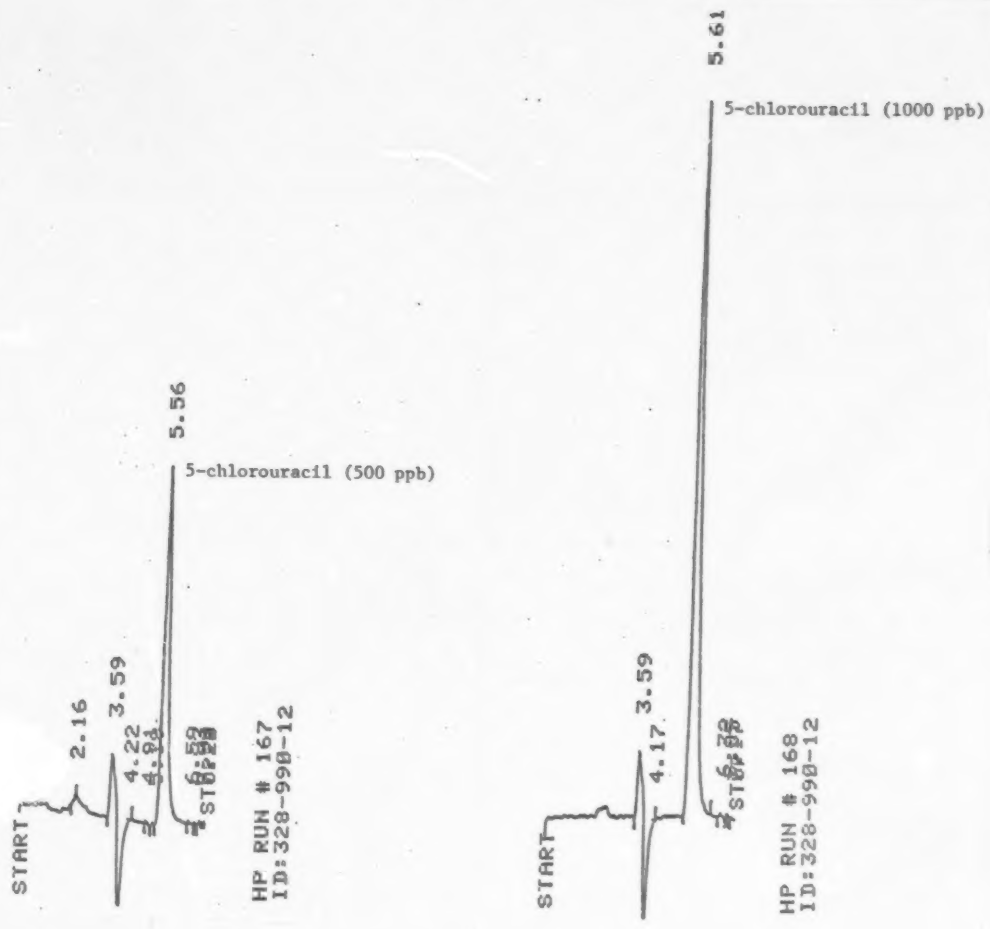

Figure 7-1. HPLC/UV chromatogram of 5-chlorouracil, Method 7-A. C18 column, mobile phase: 8% CH_3OH/92% H_2O, flow: 1.0 ml/min.

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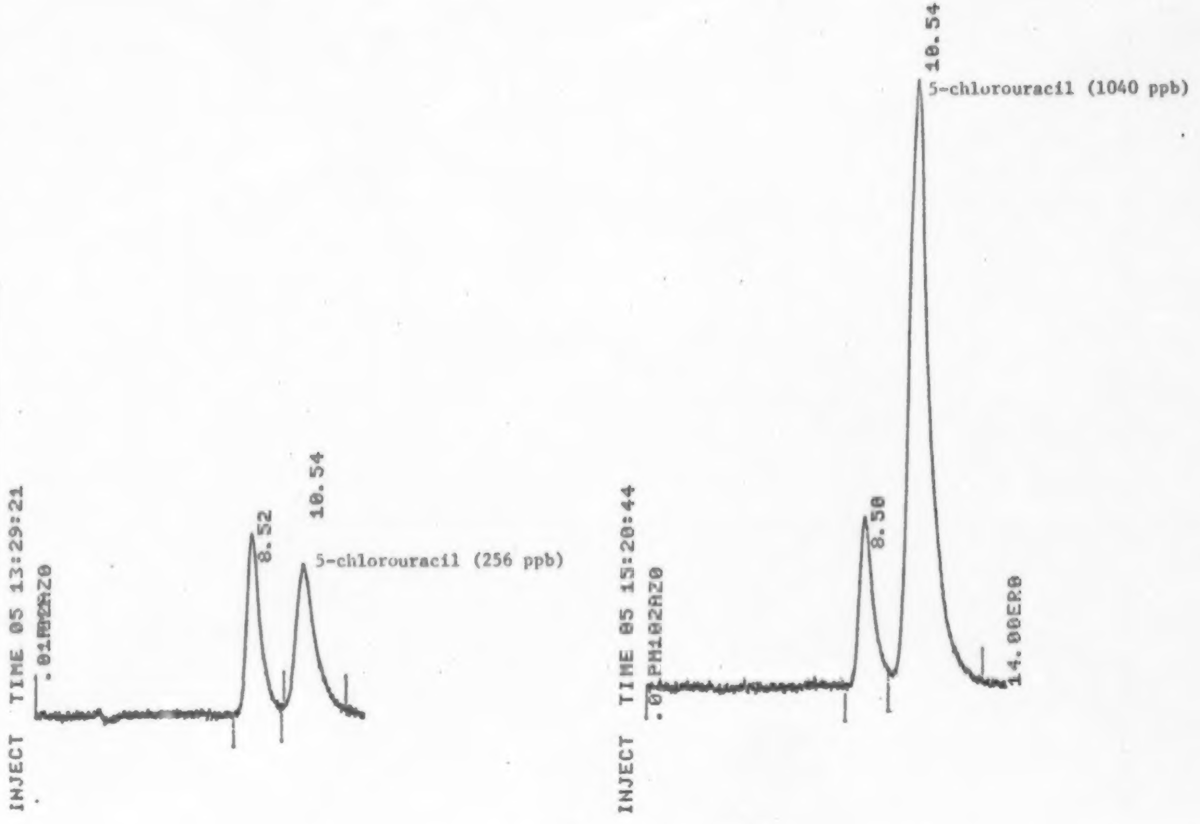

Figure 7-2. HPLC/UV chromatogram of 5-chlorouracil, Method 7-B. colum: Aminex HPX-85, mobile phase: 0.01 N H_2SO_4, flow: 0.5 ml/min.

TABLE 7-1. GROUP 7-A and 7-B - 5-CHLOROURACIL: PRECISION DATA FOR THE REVERSE PHASE AND SIZE EXCLUSION HPLC/UV ANALYTICAL METHODS

Method	5-chlorouracil Concentration (ppb)	$\overline{\text{R.T.}}$ (min)	Area Counts Mean	±	S.D.	(% CV)
7-A	20	5.41	824	±	192	(23)
7-A	50	5.42	1692	±	151	(9)
7-A	100	5.43	2884	±	294	(10)
7-A	500	5.47	15380	±	450	(3)
7-A	1000	5.52	29917	±	329	(1)
7-A	2500	5.54	86333	±	8419	(10)
7-B	52	10.48	9598	±	1048	(11)
7-B	104	10.50	21767	±	65	(0.3)
7-B	256	10.51	59550	±	3855	(6)
7-B	1040	10.53	276121	±	3084	(1)
7-B	2560	10.52	679226	±	11605	(2)

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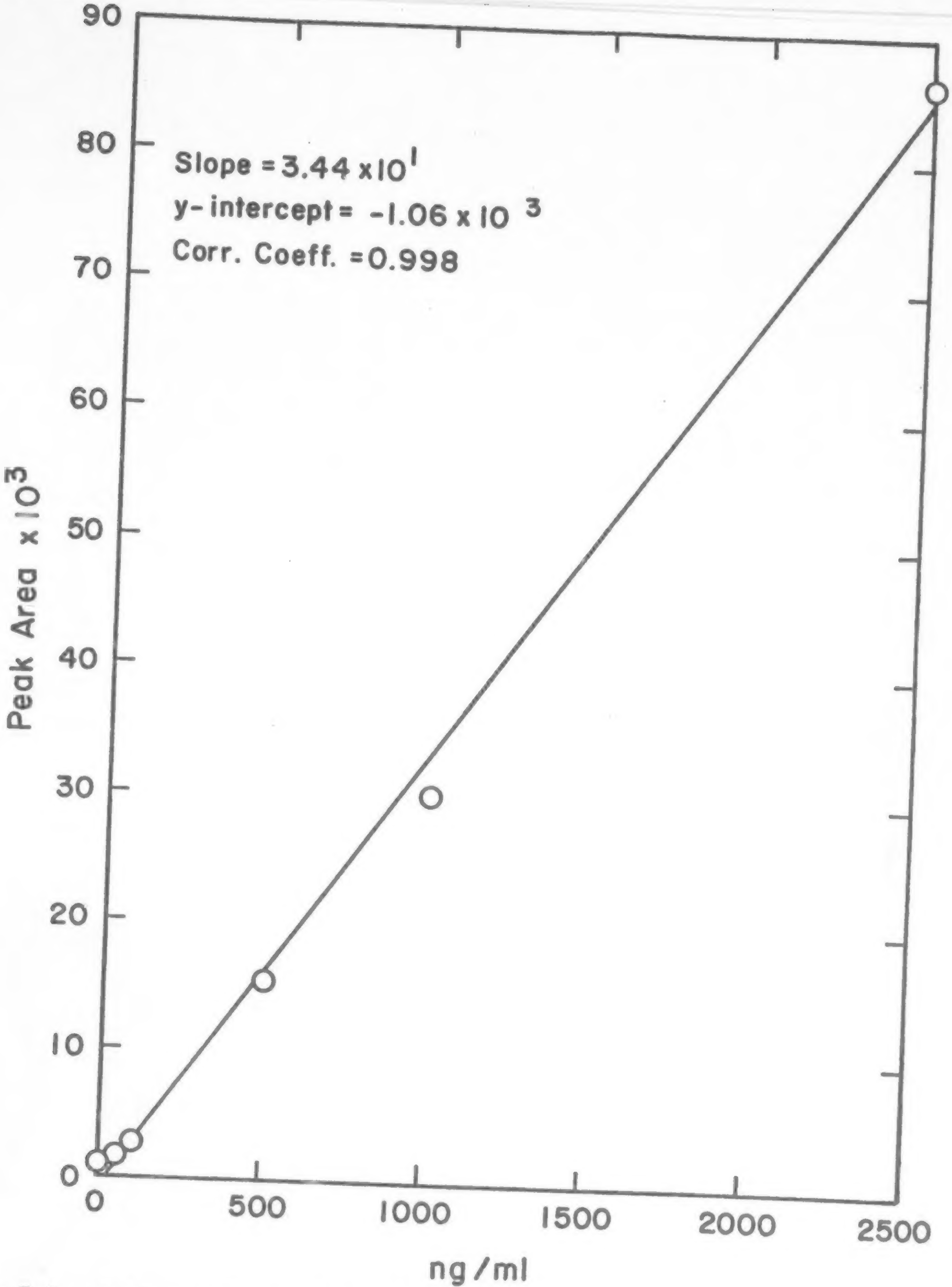

Figure 7-3. Integrated peak area versus 5-chlorouracil concentration, Method 7-A. HPLC/UV, 272 nm, mobile phase: 8% CH_3OH/92% H_2O, Column: C18.

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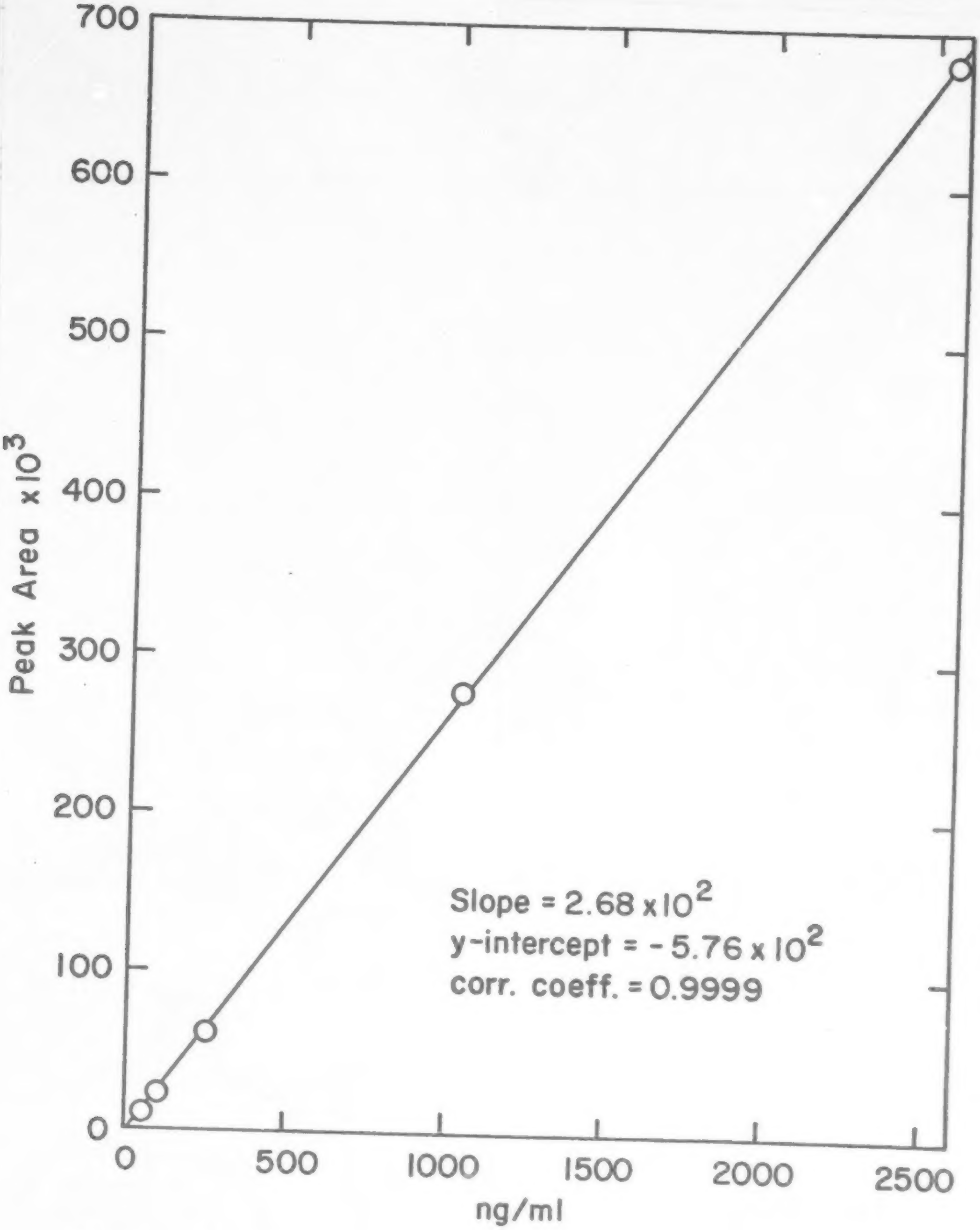

Figure 7-4. Integrated peak area versus 5-chlorouracil concentration, Method 7-B. HPLC/UV, 272 nm, mobile phase: 0.01N H_2SO_4, column: Aminex HPX-85.

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TABLE 7-2. GROUP 7-A AND 7-B - 5-CHLOROURACIL: ACCURACY AND PRECISION FOR THE REVERSE PHASE AND SIZE EXCLUSION HPLC/UV ANALYTICAL METHODS

Method	Concentration of Sample Spike	Date Analyzed	% Recovery of Spike
7-A	1000	10/20/81	104
7-A	2500	10/20/81	110
7-A	1000	11/19/81	97
7-A	250	11/19/81	95
7-A	2500	12/23/81	94
7-A	1000	12/28/81	93
			mean ± S.D. (CV) 99 ± 10 (10%)
7-B	256	04/08/82	104
7-B	1040	04/08/82	104
7-B	256	04/08/82	109
7-B	250	04/12/82	103
7-B	1000	04/12/82	98
7-B	1000	04/13/82	109
7-B	1000	04/13/82	97
7-B	1000	04/16/82	103
7-B	2500	04/16/82	87
7-B	250	04/16/82	91
			mean ± S.D. (CV) 101 ± 7 (7%)

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APPENDIX N

STANDARD OPERATING PROCEDURE FOR
GROUP 8: HUMIC ACIDS

A. Scope and Application

This method is applicable to the determination of humic acids in an aqueous matrix over the concentration range 500 ng/ml to 100,000 ng/ml. There is no interference from the other 21 compounds of interest to this study or from the acetone used to dissolve the primary stock RO spiking standards.

This method has been shown to tolerate up to 1M salts by simply cleaning the column when needed. Increased pump pressure will indicate the need for column cleaning. To clean the column, backwash with 40% CH_3CN in 0.01N H_2SO_4 at 0.1 ml/min for at least 4 hours. Further backwash with 0.05N H_2SO_4 for an additional 4 hours to regenerate the column. The column can then be returned to operating conditions for further analysis.

This method is highly pH dependent, and further study is needed to determine sensitivity and stability as a function of pH and time. This method has been evaluated only at a constant pH of 5.

B. Summary of Method

An aliquot of the aqueous sample is injected and analyzed by size exclusion HPLC with a fluorescence detector (1). An Aminex HPX-85 column with a water mobile phase provides the needed separation, and detection at $\lambda ex = 273$ nm and $\lambda em > 389$ nm provides the needed sensitivity. Quantification is based on calibration by external standards.

C. Apparatus and Materials

1. High performance liquid chromatograph (Waters Model 660 solvent programmer with Model U6K injector) interfaced to a variable excitation wavelength spectrofluorometer (Schoeffel FS970) with a means for automatic peak integration (HP 3385A Automation System or Spectra-Physics SP4100 Computing Integrator).

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1. "Advances in the Identification and Analysis of Organic Pollutants," in Water, Vol. 1, Lawrence H. Keith, Ann Arbor Sci. Pub. 1981, Mich. p. 374.

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2. Analytical column: 25 cm x 4 mm Aminex HPX-85 (Biorad)

3. Guard column: Q 15S B-19460 in H^+ form

D. Reagents

1. Water, HPLC grade

2. Acetonitrile, HPLC grade

3. 1N NaOH, in HPLC grade water

4. 1N H_2SO_4, in HPLC grade water

E. Procedure

1. Adjust sample pH to 5.

2. Inject an 80 µl aliquot of the sample into the HPLC/fluoresence system. (Samples that are cloudy or have suspended particulates should be filtered before injection.) The instrument conditions are as follows:

Instrument:	Waters HPLC (Model 660 solvent programmer with Model U6K injector) interfaced to a Schoeffel FS970 spectrofluorometer and either a HP 3385A Automation System or Spectra Physics SP4100 Computing Integrator.
Analytical column:	25 cm x 4 mm Aminex HPX-85
Guard column:	Q 15S B-19460 in H^+ form
Excitation wavelength:	273 nm
Emission filter:	389 nm
Mobile phase:	100% water
Flow rate:	0.4 ml/min
Injection volume:	80 µl

Figure 8-1 shows the separation achieved by the Aminex HPX-85 column.

4. The external standard method with integrated peak areas is used for quantification

a. Prepare a stock humic acid standard at 100 ng/µl.

   1) In a 100 ml volumetric flask, dissolve 0.01 g humic acid in pH 10 adjusted HPLC grade water.

   2) Adjust to pH 5.

   3) Dilute to volume with HPLC grade water. Final pH should be 5.

b. Prepare, from the standard stock solution five additional calibration standards in HPLC grade water at concentrations of 0.50 ng/µl, 1.0 ng/µl, 5.0 ng/µl, 10 ng/µl, and 50 ng/µl. Final pH of all calibration standards should be 5.

c. Run a linear regression analysis on the six calibration points and record the slope, y-intercept, and correlation coefficient.

d. Calculate the humic acid concentration in the unknown samples from:

$$\text{conc. (ng/µl)} = \frac{y-b}{m}$$

where:

y = integrated area of humic acids in unknown
b = y-intercept from linear regression analysis
m = slope from linear regression analysis

e. In some cases a parabolic regression analysis will provide a better fit. In this case the humic acid concentration in the unknown samples is calculated from

$$\text{conc. (ng/µl)} = \frac{-b + [(b)^2 - 4\ (c-y)\ (a)]^{\frac{1}{2}}}{2a}$$

where:

y = integrated area of humic acids in unknown
a,b,c = constants determined from the parabolic regression analysis with respect to the equation $ax^2 + bx + c = 0$

5. QA/QC

a. Generate and check calibration curves daily to confirm the model response range of the system.

b. Analyze and monitor sample blanks daily. Use as a method blank an aliquot of the HPLC water used for standard dilutions. Subtract any interference area counts from standards and samples.

c. Analyze a spiked sample for each group of five unknowns.

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F. Method Evaluation

1. Linearity and Precision

Fortified distilled water samples were used to evaluate the linearity and precision of this method. Aqueous solutions were spiked with humic acid at seven concentrations ranging from 0.5 ng/µl to 100 ng/µl. Each concentration was analyzed in triplicate with a corresponding distilled water blank. Table 8-1 indicates the method precision, and Figure 8-2 the method linearity. Figure 8-3 shows a case in which the data is still linear (correlation coefficient = 0.9965) but better fits a parabolic curve.

2. Accuracy and Precision

On this project actual RO samples spiked at various humic acid concentrations were analyzed. Results as a function of time and concentration are given in Table 8-2. Method accuracy is represented by the deviation of the mean recovery from 100%. The precision of the method over time is represented by the standard deviation and coefficient of variation of the average of the spiked recoveries.

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TABLE 8-1. GROUP 8 - HUMIC ACIDS: PRECISION DATA FOR THE SIZE EXCLUSION HPLC/FLUORESCENCE ANALYTICAL METHOD

Humic Acids Concentration (ppb)	$\overline{\text{R.T.}}$ (min)	Area Counts Mean	±	S.D.	(% CV)
500	3.47	10636	±	240	(2)
1000	3.36	24689	±	497	(2)
2000	3.27	54971	±	389	(1)
5000	3.59	141840	±	7187	(5)
10000	3.52	284635	±	11037	(4)
50000	3.47	1457996	±	16356	(1)
100000	3.45	2715320	±	116136	(4)

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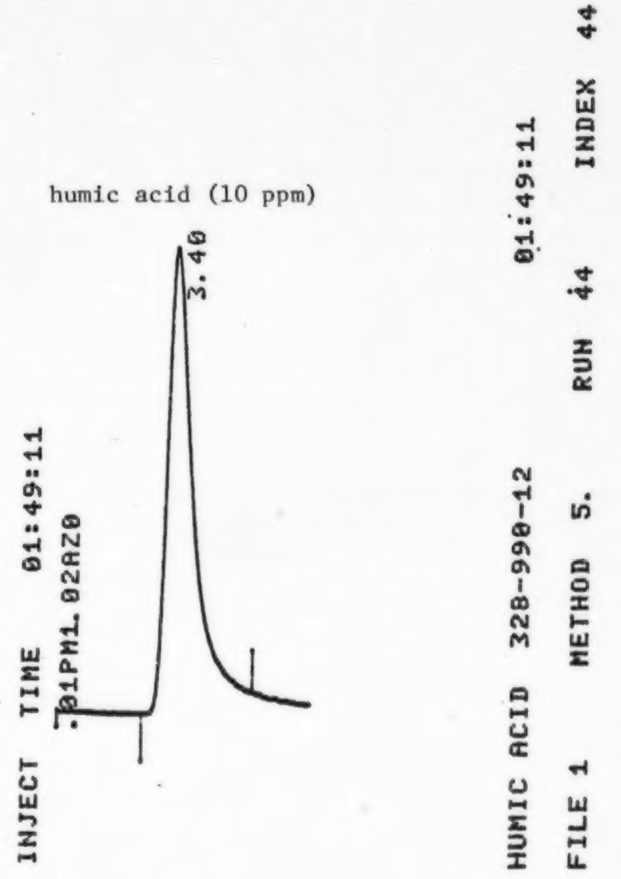

Figure 8-1. HPLC/florescence chromatogram of humic acid.
Column: Aminex HPX-85, mobile phase: H_2O, flow 0.4 ml/min.

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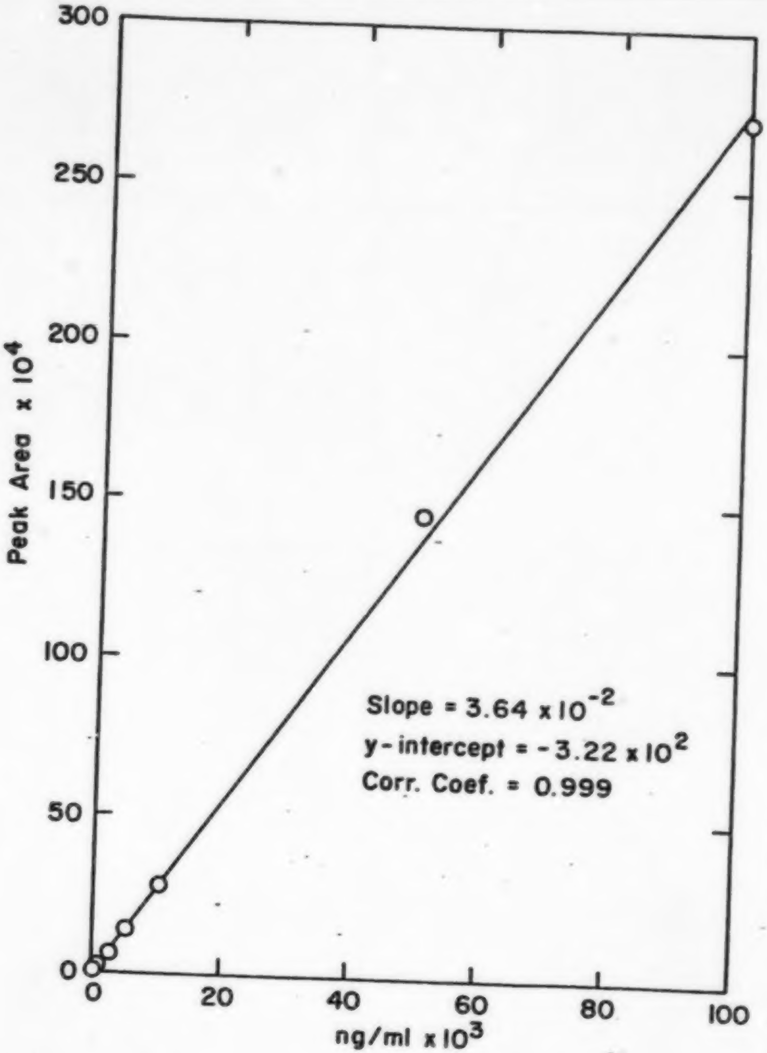

Figure 8-2. Integrated peak area versus humic acid concentration. HPLC/fluorescence, λex=273 nm, λem > 389 nm, mobile phase: H_2O; column: Aminex HPX-85.

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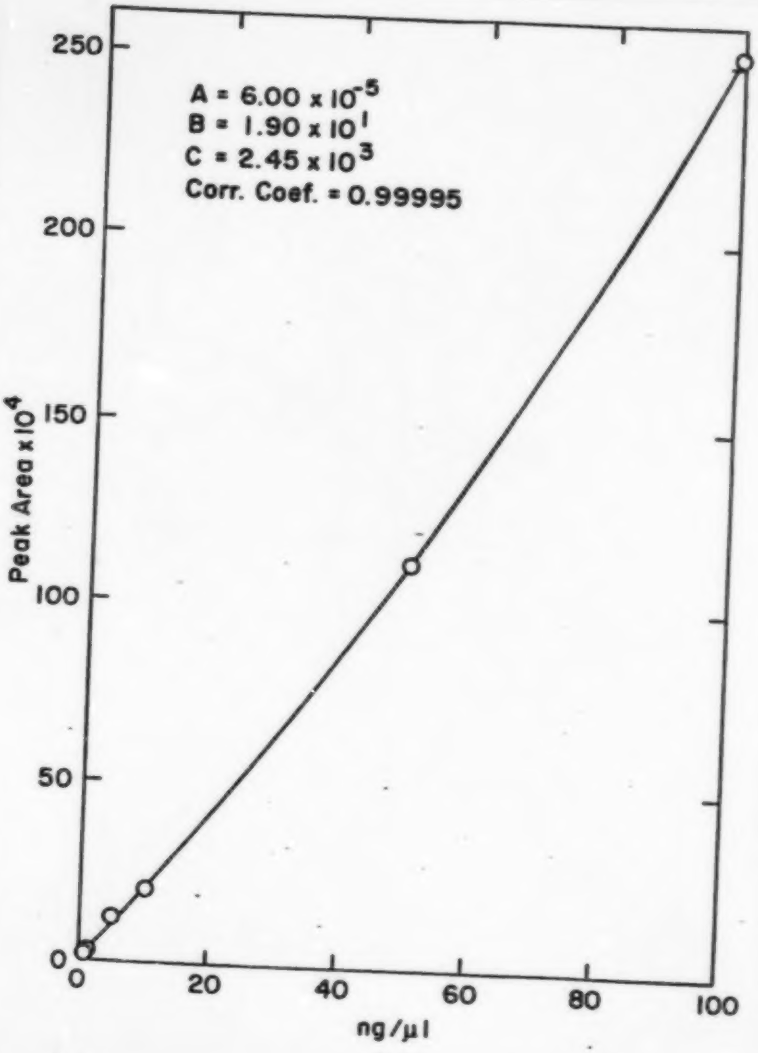

Figure 8-3. Integrated peak area versus humic acid concentration; parabolic curve fit.

TABLE 8-2. GROUP 8 - HUMIC ACIDS: ACCURACY AND PRECISION FOR THE SIZE EXCLUSION HPLC/FLUORESCENCE ANALYTICAL METHOD

Concentration of Sample Spike (ppb)	Date Analyzed	% Recovery of Spike
10,000	09/23/82	104
50,000	09/23/82	118
5,000	09/23/82	107
50,000	09/24/82	92
10,000	09/24/82	103
50,000	09/24/82	99
50,000	09/24/82	100
10,000	09/24/82	99
5,000	09/24/82	100
10,000	09/24/82	80
5,000	09/24/82	99
50,000	09/24/82	72
		mean ± S.D. (CV) 98 ± 12 (12%)

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